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Storage, Fugitive, and Secondary Sources

IT Enviroscience
Knoxville, TN

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EPA is developing new source performance standards under Section 111 of the Clean Air Act and national emission standards for hazardous air pollutants under Section 112 for volatile organic compound emissions (VOC) from organic chemical manufacturing facilities. In support of this effort, data were gathered on chemical processing routes, VOC emissions, control techniques, control costs, and environmental impacts resulting from control. These data have been analyzed and assimilated into the ten volumes comprising this report.

This volume covers emissions from storage tanks, fugitive sources (pump seals, valve seals, etc.), and secondary sources (emissions arising from treatment or disposal of process wastes).

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Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY

Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

December 1980

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INTRODUCTION

A. SOCMI PROGRAM

Concern over widespread violation of the national ambient air quality standard for ozone (formerly photochemical oxidants) and over the presence of a number of toxic and potentially toxic chemicals in the atmosphere led the Environmental Protection Agency to initiate standards development programs for the control of volatile organic compound (VOC) emissions. The program goals were to reduce emissions through three mechanisms: (1) publication of Control Techniques Guidelines to be used by state and local air pollution control agencies in developing and revising regulations for existing sources; (2) promulgation of New Source Performance Standards according to Section 111(b) of the Clean Air Act; and (3) promulgation, as appropriate, of National Emission Standards for Hazardous Air Pollutants under Section 112 of the Clean Air Act. Most of the effort was to center on the development of New Source Performance Standards.

One program in particular focused on the synthetic organic chemical manufacturing industry (SOCMI), that is, the industry consisting of those facilities primarily producing basic and intermediate organics from petroleum feedstock meterials. The potentially broad program scope was reduced by concentrating on the production of the nearly 400 higher volume, higher volatility chemicals estimated to account for a great majority of overall industry emissions. EPA anticipated developing generic regulations, applicable across chemical and process lines, since it would be practically impossible to develop separate regulations for 400 chemicals within a reasonable time frame.

To handle the considerable task of gathering, assembling, and analyzing data to support standards for this diverse and complex industry, EPA solicited the technical assistance of IT Enviroscience, Inc., of Knoxville, Tennessee (EPA Contract No. 68-02-2577). IT Enviroscience was asked to investigate emissions and emission controls for a wide range of important organic chemicals. Their efforts focused on the four major chemical plant emission areas: process vents, storage tanks, fugitive sources, and secondary sources (i.e., liquid, solid, and aqueous waste treatment facilities that can emit VOC).

B. REPORTS

To develop reasonable support for regulations, IT Enviroscience gathered data on about 150 major chemicals and studied in-depth the manufacture of about 40 chemical products and product families. These chemicals were chosen considering their total VOC emissions from production, the potential toxicity of emissions, and to encompass the significant unit processes and operations used by the industry. From the in-depth studies and related investigations, IT Enviroscience prepared 53 individual reports that were assembled into 10 volumes. These ten volumes are listed below:

Volume 1 : Study Summary
Volume 2 : Process Sources
Volume 3 : Storage, Fugitive, and Secondary Sources
Volume 4 : Combustion Control Devices
Volume 5 : Adsorption, Condensation, and Absorption Devices
Volume 6-10: Selected Processes

This volume covers the generic VOC emission studies for storage and handling emissions, fugitive emissions and secondary emissions. The focus of the reports is on control of new sources rather than on existing sources in keeping with the main program objective of developing new source performance standards for the industry. The reports do not outline regulations and are not intended for that purpose, but they do provide a data base for regulation development by the EPA.

REPORT 1

STORAGE AND HANDLING

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Research Triangle Park, North Carolina

September 1980

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch² (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1×10^{12} grams
G	giga	10^{9}	1 Gg = 1×10^{9} grams
M	mega	10^{6}	1 Mg = 1×10^{6} grams
k	kilo	10^{3}	1 km = 1×10^{3} meters
m	milli	10^{-3}	1 mV = 1×10^{-3} volt
μ	micro	10^{-6}	1 μg = 1×10^{-6} gram

II. CHARACTERIZATION AND DESCRIPTION

A. INTRODUCTION

The synthetic organic chemical manufacturing industry (SOCMI) is a segment of the domestic chemical industry that produces the 350 to 400 basic and intermediate organic chemicals used to produce other, finished chemicals and products. Organic chemicals not included in the SOCMI are refinery by-products, coal tar and other "naturally" derived organic chemicals, polymers, and end-use (finished) organic chemicals.

The data base for the synthetic organic chemicals manufacturing industry (SOCMI) for this report was compiled from state emissions inventory questionnaires (EIQ) and information obtained from plant site visits.[1]

Texas and Louisiana State EIQs supplied an estimated 80% of the tanks in the data base, which covered approximately 4000 tanks used for the storage of organic chemicals.[1,2] The use of only two state EIQs to supply the bulk of the storage tank data base was reasonable since production in these states is estimated to be 65 wt % of the total SOCMI production.[3]

The data collected included various tank characteristics, type, use, and contents. This information was assembled on forms and stored in a computer data base developed by Mitre Corp., Metrek Division, McClean, VA, who used the MRI system 2000 to manage the data base. The program has the capability of computing emissions from each tank and of characterizing the data base in terms of various input parameters, such as tank size, vapor pressure, tank type, and emissions.[4]

Extrapolation of the data base to the SOCMI was done on a weight basis. It was estimated that the 4000 tanks represented approximately 20% of the total SOCMI production. Individual tanks in the data base were assigned to a specific process at a given site. The production from each process was summed to yield a total production for the data base. A comparison of the reported SOCMI production[5] with the industrial production derived from the data base indicated that a scaleup factor of 5.0 was required for completion of the SOCMI storage characterization projection for 1977.

B. STORAGE TANKS

There are three basic designs for tanks storing volatile organic compounds (VOC) in the SOCMI: fixed roof, floating roof [open or covered (internal)], and pressure (low or high) vessel. These tanks are usually loaded by submerged or bottom filling and are unloaded into marine vessels, tank cars, tank trucks, or pipe lines. It is estimated that 20,300 VOC storage tanks, each with a capacity of 3.8 m^3 or greater, are located throughout the United States and Puerto Rico. The total VOC storage volume is estimated to be 11,650 X 10^3 m^3 (see Table II-1 and Fig. II-1). Approximately 14,800 fixed-roof tanks make up 61% (7100 X 10^3 m^3) of the total storage volume, 700 floating-roof tanks make up 20% (2340 X 10^3 m^3), and 4800 pressure tanks make up the remaining 19% (2210 X 10^3 m^3).

The tanks are used for storing a variety of materials: raw materials, intermediates, final product, and/or usable by-products, as well as waste tars, residues, and nonusable by-products. It is estimated (see Fig. II-2) that of the total number of tanks the feed storage tanks comprise 23%, or 27% of the total storage volume; product storage tanks comprise 45%, or 53% of the total storage volume; intermediate tanks comprise 29%, or 17% of the storage volume; and waste storage tanks comprise 3% of both the total number of tanks and the total storage volume.

The vapor pressure of the material stored is a major factor in the choice of tank type used. Table II-2 gives the number of tanks and the total volume by vapor pressure of the chemicals stored in each of the three basic tank types. Fixed-roof tanks are normally used for storing materials with vapor pressures up to 34.5 kPa, floating-roof tanks when vapor pressures are in the range of 6.9 to 34.5 kPa, and pressure tanks when vapor pressures are greater than 51.7 kPa. Other factors, e.g., material stability, safety hazards, health hazards, and multiple use, can also affect the choice of tank type for a particular organic chemical.

Small tanks are commonly used for high-turnover service, such as intermediate storage. Very large tanks are used for low-turnover service, such as terminal product storage. A correlation has been found between tank turnovers and tank size. In general, as the tank size increases, the turnovers decrease. For very small tanks (less than 35 m^3) turnovers can approach 700 per year. Very

Table II-1. Number of Tanks and Storage Volume by Tank Size*

Tank Size (m^3)	Fixed Roof		Floating Roof		Pressure Vessel		Total	
	No.of Tanks	Storage Volume (m^3)	No.of Tanks	Storage Volume (m^3)	No.of Tanks	Storage Volume (m^3)	No.of Tanks	Storage Volume (m^3)
4 to 45	5,105	124,000	0	0	1,370	34,000	6,475	158,000
45 to 90	3,010	205,000	10	600	785	54,000	3,805	259,600
90 to 190	1,980	282,000	40	6,000	1,190	153,000	3,210	441,000
190 to 380	1,375	396,000	85	26,000	450	119,000	1,910	541,000
380 to 950	1,560	968,000	140	86,000	330	209,000	2,030	1,263,000
950 to 1900	975	1,416,000	95	140,000	410	473,000	1,480	2,029,000
1900 to 3800	520	1,428,000	125	331,000	125	283,000	770	2,042,000
3800	290	2,278,000	175	1,752,000	125	887,000	590	4,917,000
Total	14,815	7,097,000	670	2,341,600	4,785	2,212,000	20,270	11,650,600

*See ref. 1 (includes only tanks with capacity greater than 3.8 m^3).

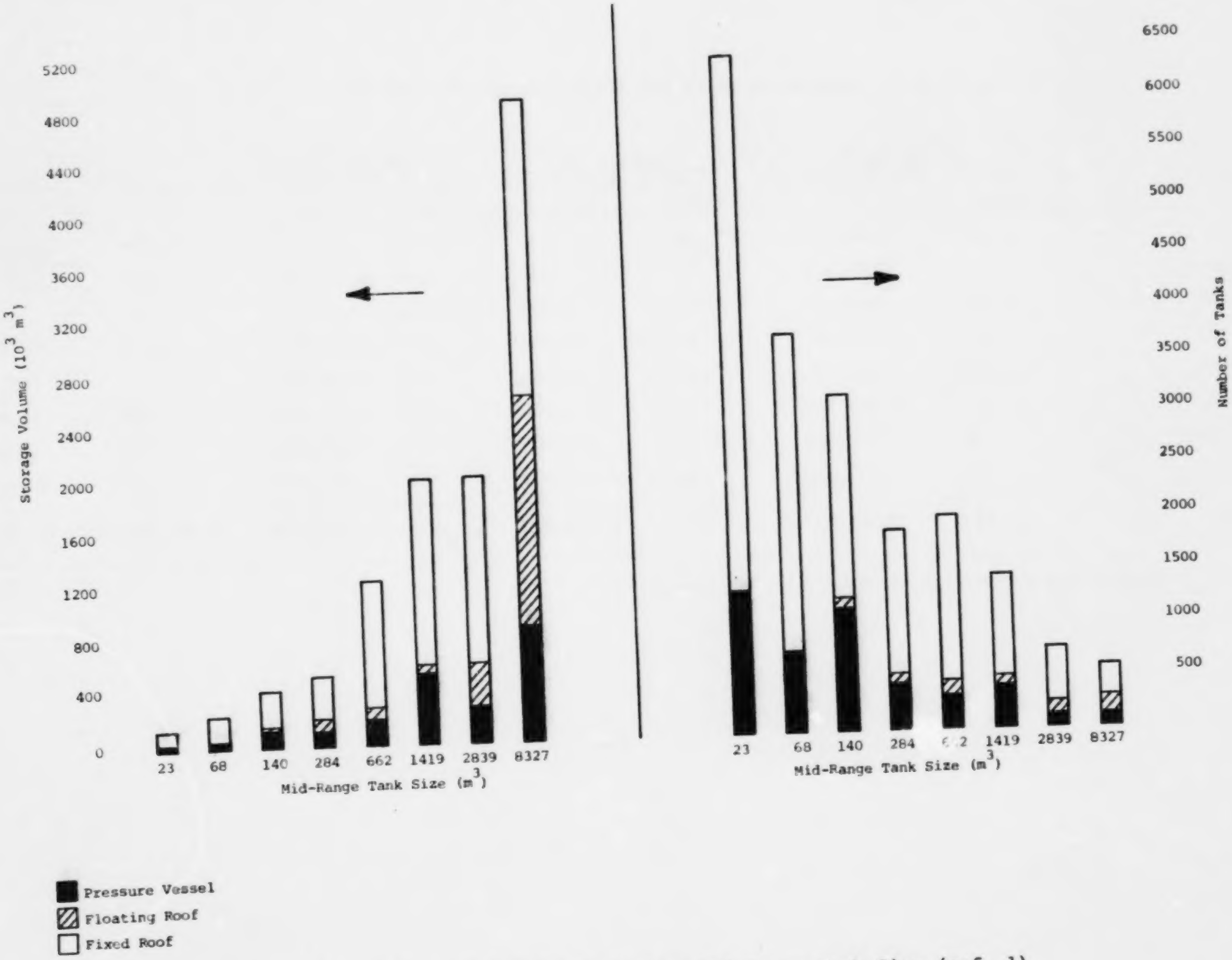

Fig. II-1. Number of Tanks and Storage Volume vs Tank Size (ref. 1)

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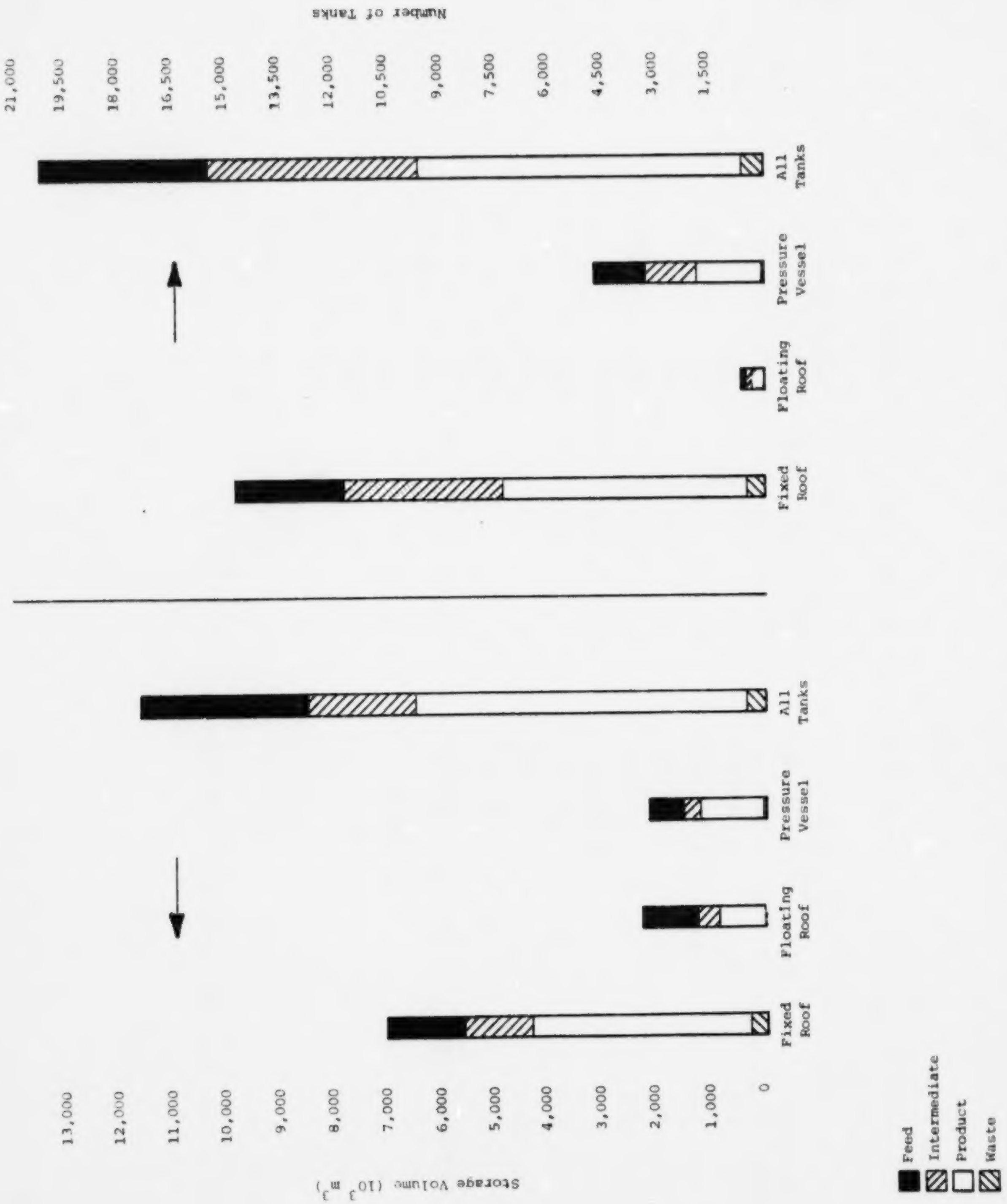


Fig. II-2. Number of Tanks and Storage Volume vs Tank Type and Use

Table II-2. Number of Tanks and Storage Volume by VOC Vapor Pressure*

Vapor Pressure (kPa)	Fixed Roof		Floating Roof		Pressure Vessel		Total	
	No. of Tanks	Storage Volume (m^3)	No. of Tanks	Storage Volume (m^3)	No. of Tanks	Storage Volume (m^3)	No. of Tanks	Storage Volume (m^3)
0.0001 to 1.4	7,400	2,718,000	55	134,000	330	25,000	7,785	2,877,000
1.4 to 3.5	2,070	1,035,000	55	71,000	180	20,000	2,305	1,126,000
3.5 to 6.9	1,955	951,000	45	144,000	140	59,000	2,140	1,154,000
6.9 to 10.3	980	653,000	35	319,600	140	45,000	1,155	1,017,600
10.3 to 20.7	1,475	1,188,000	305	1,009,000	405	43,000	2,185	2,240,000
20.7 to 34.5	600	344,000	140	602,000	225	49,000	965	995,000
34.5 to 51.7	165	102,000	20	41,000	190	31,000	375	174,000
51.7 to 69.0	90	47,000	0	0	155	108,000	245	155,000
69.0 to 103.4	80	59,000	15	21,000	230	63,000	325	143,000
103.4 to 172.3	0	0	0	0	390	390,000	390	390,000
172.3 to 344.7	0	0	0	0	945	501,000	945	501,000
344.7 to 517.0	0	0	0	0	600	682,000	600	682,000
517.0+	0	0	0	0	855	196,000	855	196,000
Total	14,815	7,097,000	670	2,341,000	4,785	2,212,000	20,270	11,650,600

*See ref. 1 (includes only tanks with capacity greater than 3.8 m^3).

large tanks (greater than 7000 m^3) normally have 12 turnovers or less per year. All the data collected and the smooth curve fitting the correlation appear in Fig. II-3.[1]

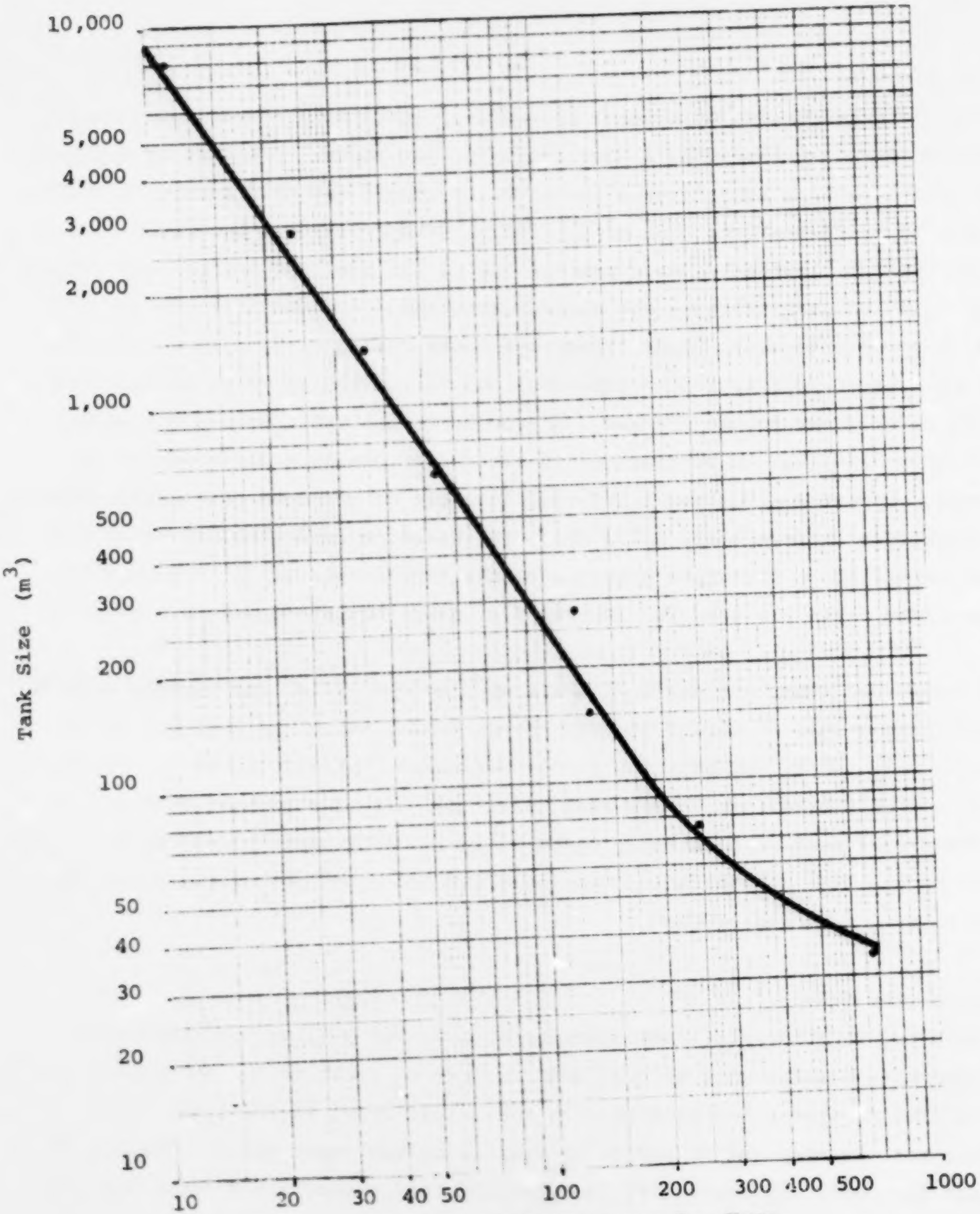
1. Fixed-Roof Tanks

Fixed-roof tanks consist of a steel cylindrical shell with a stationary roof. The design may vary from cone-shaped roofs to flat roofs. The tank is designed to operate at only slight internal pressure or vacuum and thus is highly susceptible to emissions from breathing, filling, and emptying. The fixed-roof tank is the least expensive to construct and of all the tank designs now in use is generally considered to be the minimum acceptable standard for storage of volatile organic liquids. Some fixed-roof tanks are equipped with a conservation vent, which is a type of a pressure- and vacuum-relief valve designed to contain minor vapor volume changes. The conservation vent reduces the amount of breathing loss by not venting unless the design pressure differential is exceeded. However, since the fixed-roof tank can be operated only within very small pressure differentials (±0.2 kPa), the emission reduction may be as low as 5%, depending on the vapor pressure of the stored material.[6,7] Generally, conservation vents are used for low-vapor-pressure VOC storage (<10.5 kPa).[7]

Most fixed-roof tanks are small; 55% are smaller than 91 m^3 and contain only 5% of the total volume of liquid stored. Large tanks, 946 m^3 or greater, which comprise only 12% of the existing fixed-roof tanks, contain 72% of the total volume of VOC stored (see Tables II-1 and II-2). It is estimated that 36% of the fixed-roof tanks (5345 tanks) contain liquids with vapor pressures in excess of 3.5 kPa. These tanks comprise 47% (3344×10^3 m^3) of the total VOC fixed-roof tank storage volume.

2. Floating-Roof Tanks

The open-top floating-roof tank consists of a welded cylindrical steel wall equipped with a metal deck or roof that is free to float on the surface of the stored liquid, rising and falling with the liquid level in the tank. This feature reduces evaporation losses by minimizing the vapor space. The liquid surface is completely covered by the floating roof except for a small annular space between the roof and the shell. A sliding seal attached to the floating



021 Fig. II-3. Average Number of Turnovers of VOC Storage Tanks vs Tank Size (ref. 1)

roof fits against the tank wall and covers the remaining area. The primary source of VOC emissions is through gaps in this seal.

Most emissions through the seal are attributable to wind effect. Wind blowing across the tank creates pressure differentials around the edges of the floating roof so that air flows into the seal on the leeward side, and air saturated with VOC flows out on the windward side. Improper or loose fit of the seal significantly increases the emission rate.[8]

The internal-floating-roof tank is a fixed-roof tank that has an internal roof or deck floating on the liquid surface. If the internal roof is made of steel, the tank is referred to as a "covered-floating-roof" tank. If the roof is made of a material other than steel, the tank is referred to as an "internal-floating-cover" tank.

Like the open-top floating roof, the internal floating roof has an attached sliding seal that fits against the tank wall. Antirotational guides are provided to maintain proper roof alignment. Special vents are installed on the fixed roof or on the walls at the top of the shell to minimize the flammable vapor concentrations in the vapor space. The fixed roof protects the floating roof or deck and the seal from deterioration due to meterological effects, eliminates the possibility of the roof sinking because of excess rain or snow loads, and decreases the wind-induced pressure differential around the roof.

Floating-roof tanks comprise only 3.0% of the total number of storage tanks in the industry. They generally have very large capacities, with 80% of the total having capacities in excess of 379 m^3 and 26% in excess of 3785 m^3. The majority (72%) are used for storing VOC with vapor pressures of 6.9 to 34.5 kPa. This comprises 82% (1930 X 10^3 m^3) of the total floating-roof tank storage volume.[1]

3. Pressure Tanks

Pressure tanks are designed to withstand relatively large internal pressures. They are generally used for storing highly volatile and/or toxic materials and are constructed in various sizes and shapes, depending on the operating pressure range. Noded spheroid and hemispheroid shapes are generally used for

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low-pressure tanks (117 to 207 kPa); horizontal cylinder and spheroid designs are generally used for high-pressure tanks (up to 1827 kPa). Because pressure tanks are generally operated in a closed system at the pressure of the stored material, losses are not generally incurred. Pressure tanks with inert gas blanketing are a minor exception and are discussed in Sect. IV.

C. LOADING AND HANDLING

Loading and transportation operations of the SOCMI are very similar to those of the petroleum liquids (refinery) industry except that they are on a relatively smaller bulk scale. Synthetic organic chemicals are transported from the initial producing sites to consumers. The consumers in most cases are other industrial organic chemical producers, who use the basic and intermediate organic chemicals as raw materials to manufacture additional intermediates or finished products.

An estimated 33,925,000 Mg (35,390 X 10^3 m^3) of synthetic organic chemicals was shipped in 1976.[5] Water transportation was the type of shipment most often used, accounting for 50% (17,695 X 10^3 m^3) of the total volume; tank-car rail shipments accounted for 30% (10,617 X 10^3 m^3) of the total, and truck shipments for the remaining 20% (7078 X 10^3 m^3).[2] The quantities of chemicals at specific ranges of vapor pressure that were shipped were estimated on the basis of proportional volume and vapor pressure ranges of the chemicals stored. Shipment volumes based on the percentages given in Table II-2 are shown in Table II-3.

An estimated 81% of all VOC shipped have a vapor pressure of less than 34.5 kPa. Approximately 14.8% (5246 X 10^3 m^3) have a vapor pressure of greater than 103.4 kPa and are assumed to be stored and loaded in closed systems[2] with negligible VOC loss.

Transit losses were calculated by computing a breakdown of the time required for each shipment based on the 1972 Census of Transportation.[9] The time required for most shipments (45 wt %) (see Table II-4) is approximately one day.

Table II-3. Vapor Pressure and Volume of Synthetic Organic Chemicals Shipped*

Vapor Pressure (kPa)	Percentage of Volume Stored	Volume Shipped (X 10^3 m^3)
0.001 to 1.4	24.7	8,743
1.4 to 3.5	9.7	3,429
3.5 to 6.9	10.0	3,543
6.9 to 10.3	8.8	3,111
10.3 to 20.7	19.4	6,866
20.7 to 34.5	8.6	3,043
34.5 to 51.7	1.5	530
51.7 to 69.0	1.3	454
69.0 to 103.4	1.2	424
>103.4	14.8	5,246
Total	100.0	35,389

*Refs. 1 and 5.

Table II-4. Time Required for Shipments[a]

Fraction[b] of a Week	Percentage[c] of Material Shipped	Volume Shipped (X 10^3 m^3)
1/7	45.0	15,925
2/7	24.0	8,493
3/7	14.0	4,955
7/7	17.0	6,016
Total	100.0	35,389

[a] Refs. 1, 5, and 8.

[b] Ref. 8.

[c] Ref. 1.

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D. REFERENCES*

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2. Texas/Louisiana State Emission Inventory Questionnaires (1975) (on file at EPA, ESED, Research Triangle Park, NC).

3. 1976 Directory of Chemical Producers, United States of America, Stanford Research Institute, Menlo Park, CA (1977).

4. E. G. Webster, Description of the Chemical Storage Tank Emissions (Tankemis) Data Base, Working Paper No. 12993, Mitre Corp., Metrek Division, Mclean, VA (May 1978).

5. Synthetic Organic Chemicals, 1976 United States Production and Sales, United States International Trade Commission, GPO, Washington (1977).

6. C. C. Masser, "Storage of Petroleum Liquids," p 4.3-1 in Compilation of Air Pollutant Emission Factors, AP-42, Part A, 3d ed. (August 1977).

7. Control of Volatile Organic Compounds from Storage of Petroleum Liquids (draft copy) (prepared by EPA, ESED, Research Triangle Park, NC) (November 1977).

8. C. C. Masser, "Storage of Petroleum Liquids," pp. 4.3-5 in Compilation of Air Pollutant Emission Factors, AP-42, Part A, 3d ed. (August 1977).

9. Cited in Kline Guide to the Chemical Industry, 3d ed., p 58, edited by M. K. Meegen, Charles H. Kline and Co., Inc., Fairfield, NJ, 1977.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. EMISSIONS

A. SOURCES

1. Storage Tanks[1]

There are five emission sources that need to be considered in organic chemical storage: fixed-roof breathing losses, fixed-roof working losses, floating-roof standing-storage losses, floating-roof withdrawal losses, and pressure-tank losses.

Fixed-roof breathing losses occur when VOC is expelled from a tank because vapors expand and contract as a result of a diurnal temperature change or barometric pressure changes and additional VOC vaporization.

Fixed-roof working losses result from VOC being expelled from a tank during filling and emptying operations. During the filling operation vapor is displaced by the incoming liquid, and during the emptying operation air is drawn into the tank and becomes saturated with organic vapor and is discharged during the next filling.

Floating-roof standing storage losses occur when VOC is expelled from the tank. The primary source of this loss is a defective fit of the seal and shoe to the tank wall, which exposes some liquid surface to the atmosphere.

Floating-roof withdrawal losses occur when VOC is evaporated from the liquid film that wets the tank wall while the roof descends during emptying operations. This loss will be small compared to the other types of losses if the number of tank turnovers is low.

No VOC losses will be experienced from pressure-tank operation under normal conditions. Losses may occur if an inert-gas pad is used for safety or operating reasons or if the pressure inside the tank exceeds the relief (safety) operating pressure.

The following main-storage operating factors affect VOC loss: vapor pressure of the liquid stored, temperature changes in the tank, tank vapor space (tank outage), tank diameter, frequency of turnovers, mechanical condition of tank and seals, tank type, tank color, and weather conditions.

2. Loading and Handling[2]

There are three emission sources from the transportation of volatile synthetic organic chemicals: loading losses, transit losses, and ballasting losses. Both loading and transit losses occur when VOC is transported by marine vessels, tank cars, or tank trucks. With marine vessels there can also be ballasting losses. VOC losses from pipe lines are negligible under normal operating conditions.

Loading losses are the primary source of emissions from marine vessel, tank-car, and tank-truck operations and occur when vapors residing in empty cargo tanks are displaced to the atmosphere by the liquid being loaded. These vapors are a mixture of the vapors formed in the empty tank by evaporation of residual product from a previous load and those generated in the tank as a new product is being loaded.

The total evaporative loss from loading operations is a function of the physical and chemical properties of the previous and new cargos, the method used for loading or unloading the cargos, and the service history of the cargo carrier ("clean tank; normal, dedicated service; or dedicated, vapor balance service").

Transit losses will occur if vapor is expelled because of temperature and barometric pressure changes while the cargo tank is en route. These transit losses are eliminated if closed pressure carriers are used.

An additional practice, specific to marine vessels, that increases shipping losses is ballasting. After a cargo is unloaded, the empty tanker will normally carry several cargo tanks filled with water to improve stability during the return voyage. VOC vapors remaining in the empty tanks are expelled when the ballast water is added.

B. CALCULATIONS

1. Storage Tanks

Emissions from organic chemicals stored in fixed-roof and floating-roof tanks were calculated with use of the following empirical equations.

a. Fixed-Roof Tanks——Breathing losses and working losses occur from storage of chemicals in fixed-roof tanks. The AP-42 emissions equations for breathing and working losses were used to estimate emissions from fixed-roof tanks.[3] However, breathing losses calculated with these equations were discounted by a factor of 4 based on test results reported by EPA,[4] the Western Oil and Gas Association (WOGA),[5] and the German Society for Petroleum Science and Carbon Chemistry (DGMK).[6] These results indicate that AP-42 tends to overestimate the actual breathing losses from fixed-roof tanks by a factor of roughly 4. The working losses have not been adjusted, because initial testing indicates that AP-42 is fairly accurate for this estimation.

Breathing losses——The following equation can be applied to all fixed-roof tanks and includes the assumption that no conservation vent is installed on the tank:

$$L_B = 9.15 \times 10^{-6}\ M\ {\frac{P}{14.7 - P}}^{0.68}\ D^{1.73}\ H^{0.51}\ \Delta T^{0.5}\ F_p C K_c \quad ,$$

where

L_B = fixed roof breathing loss (Mg/yr) ,
M = molecular weight of vapor in storage tank (lb/lb mole),
P = true vapor pressure at bulk liquid conditions (psia),
D = tank diameter (ft),
H = average vapor space height (ft; used 1/2 tank height),
ΔT = average diurnal temperature change (°F; used 20°F),
F_p = paint factor (dimensionless, assuming a white tank in good condition; factor = 1),
C = adjustment factor (dimensionless) for large-diameter tanks ($D \geq 30$ ft), c = 1; for small-diameter tanks (less than 30 ft) = $0.0771\ (D) - 0.0013\ (D^2) - 0.1334$ (ref 7),
K_c = crude-oil factor (dimensionless; used 1.0).

The average diurnal (day/night) temperature change is variable and can be determined from National Weather Service data for a plant at a specific geographic location.

The paint factor (F_p) for fixed-roof tanks, taken from AP-42, can be obtained for the specific example given in Table A-1 (Appendix A) of AP-42.

Working losses[3]——The following equation can be applied to all fixed-roof tanks with or without conservation vents:

$$L_w = 1.09 \times 10^{-8} MPK_nK_c \; VN \; ,$$

where

L_w = fixed-roof working loss (Mg/yr),
N = turnovers per year,
K_n = turnover factor (dimensionless)
= $(180 + N)/6N$ for $N > 36$ and = 1 for $N \leq 36$,
V = tank volume (gal),
M, P, and K_c = same as for fixed-roof breathing losses.

Tank turnovers per year, if not stated, can be obtained by dividing the annual throughput through the tank by the tank's capacity.

b. Floating-Roof Tanks——Standing-storage losses and withdrawal losses were calculated for floating-roof tanks as follows.

Standing-storage losses[9]——The following equation can be applied to both open-top and internal-floating-roof tanks with single primary seals:

$$L_s = 0.00921\, M \, {\frac{P}{14.7 - P}}^{0.7} D^{1.5} \, v_w^{\;0.7} \, K_tK_sK_pK_c \, \frac{365}{2205} \; ,$$

where

L_s = floating-roof standing-storage loss (Mg/yr),
v_w = average wind velocity (miles/hr; used 9.0),
K_t = tank type factor (dimensionless; used 0.045 based on welded tank),

K_s = seal factor (dimensionless; used 1.0),
K_p = paint factor (dimensionless; used 0.9 based on white paint),
M, P, D, and K_c = same as for fixed-roof breathing losses.

An average wind speed (v_w) should be used for determining losses from open-top floating-roof tanks. A wind speed of 4 mph should be used for calculating losses from internal-floating-roof tanks.

The factors K_t, K_s, and K_p depend on the type of tank construction, tank seal, and paint used, respectively. Table A-2 gives the values for these factors, taken from AP-42.

Withdrawal losses——The following equation[10,11] can be applied to both internal- and open-top floating-roof tanks that are equipped with either a primary seal or a primary and a secondary seal:

$$L_{wd} = 0.000198 \text{ DTHd } \frac{1}{2205} ,$$

where

L_{wd} = floating roof withdrawal loss (Mg/yr),
D = tank diameter (ft),
T = turnovers (per yr),
H = tank height (ft),
d = density of stored liquid at bulk liquid conditions (lb/gal; used 8.0).

Floating-roof-tank emissions can also be estimated with the equations shown in Appendix B. These equations were not used to estimate emissions for this report since they were not available when the original report was issued and sufficient time was not available to incorporate them into this revision. The equations were derived from a pilot-test tank study conducted for the EPA.[12]

c. Pressure Vessels——Pressure tanks were considered to be closed systems with no estimated VOC emissions.

Problems may exist in applying these correlations to organic chemical storage because they are based on empirical relationships developed primarily from data on gasoline storage.[13] Most stored organic chemicals have vapor pressures outside the range of the data base used by the American Petroleum Institute. However, in the absence of correlations developed specifically for volatile synthetic organic chemicals, the existing equations were considered to be adequate for this study.

2. Loading and Handling

Emissions from organic chemical transportation were calculated with the following empirical equations.

a. Loading Losses[14]——The following equation can be applied to tank-car, tank-truck, and marine-vessel loading and assumes that no supplemental emission control device is in use:

$$L_L = 12.46 \frac{SPM}{T} \frac{V}{1000} \frac{1}{2205} ,$$

where

L_L = loading loss (Mg/yr),

S = saturation factor (dimensionless; used 1.0 for tank truck and tank car and 0.2 for marine vessels),

P = true vapor pressure of the liquid loaded (psia),

M = molecular weight of vapors (lb/lb mole),

T = bulk temperature of liquid loading [°R; used 540°R (80°F)],

V = volume loaded (gal/yr).

The saturation (S) factor represents the expelled vapor's fractional approach to saturation and accounts for the variations observed in emission rates from the different unloading and loading methods. An S factor of 1.0 for tank cars and tank trucks and an S factor of 0.2 for marine vessels give an average estimate of emissions for the industry, which uses a variety of loading methods, with no add-on emission control devices assumed to be in use. Table A-3 gives the S values to be used for specific loading methods, taken from AP-42.[14]

b. Transit Losses[14]——The following equation can be applied to tank-car, tank-truck, and marine-vessel transport and assumes that the carrier is not a pressure vessel:

$$L_t = 0.1\ PW\ \frac{V}{1000}\ \frac{1}{2205}\ T\ ,$$

where

L_t = transit loss (Mg/yr),
P = true vapor pressure of the liquid loaded (psia),
W = density of condensed vapor (lb/gal; used 8.0),
V = volume transported per year (gal/yr),
T = fraction of a week required for transport.

Ballasting losses could not be estimated because data were not available on chemical transport by ships that are ballasted. This is not expected to be a major emission for organic chemical transportation.

C. INDUSTRY EMISSIONS

SOCMI VOC emissions from both storage and loading are presented in two ways: (1) Uncontrolled VOC emissions are calculated with the equations described in Sect. B. Uncontrolled VOC emissions are defined as those emissions that would occur as a result of no add-on controls being used on storage tanks or during loading operations. (2) Current or present VOC emissions from storage and loading are calculated by estimating the number and operating efficiency of add-on controls currently in use and applying them to the uncontrolled emissions. Because floating-roof tanks are VOC emission control devices, current and uncontrolled VOC emission quantities from floating-roof tanks are the same. Pressure tanks are considered to be closed systems with no estimated VOC emissions.

1. Uncontrolled Emissions (1977)

a. Storage Tanks -- Uncontrolled VOC emissions from existing fixed-roof tanks are calculated to be 45,122 Mg/yr and for floating-roof tanks to be 1851 Mg/yr, for a projected total of 46,973 Mg/yr.[15] Tables III-1 and III-2 show the distribution of the calculated emissions by tank capacity and vapor pressure, respectively.

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Table III-1. 1977 Storage-Tank VOC Emissions by Tank Size and Type[a] (Assuming No Controls)

Tank Size[b] (m^3)	Fixed-Roof Tanks		Floating-Roof Tanks[d]		Total[e]	
	No. of Tanks	Emissions[c] (Mg/yr)	No. of Tanks	Emissions[c] (Mg/yr)	No. of Tanks	Emissions[c] (Mg/yr)
4 to 40	4,495	2,483	0	0	4,495	2,483
40 to 75	2,825	2,860	10	7	2,750	2,867
75 to 115	1,425	1,639	0	0	1,360	1,639
115 to 150	550	1,754	15	7	625	1,761
150 to 190	800	1,083	25	15	915	1,098
190 to 380	1,375	4,024	85	209	1,460	4,233
380 to 950	1,560	5,710	140	157	1,700	5,867
950 to 1900	975	7,991	95	131	1,070	8,122
1900 to 3800	520	9,528	125	417	645	9,945
>3800	290	8,050	175	908	465	8,958
Total	14,815	45,122	670	1,851	15,485	46,973

[a] Includes only tanks with capacity greater than 4.0 m^3.

[b] See ref 15.

[c] Calculated from equations detailed in this section (III.B).

[d] Floating-roof tanks are actually control devices and therefore have no uncontrolled VOC emissions.

[e] Emissions from pressure vessels assumed to be negligible.

Table III-2. 1977 Storage-Tank VOC Emissions by Material Vapor Pressure and Tank Type[a] (Assuming no Controls)

Vapor Pressure[b] (kPa)	Fixed-Roof Tanks		Floating-Roof Tanks[d]		Total[e]	
	No. of Tanks	Emissions[c] (Mg/yr)	No. of Tanks	Emissions (Mg/yr)	No. of Tanks	Emissions[c] (Mg/yr)
0.001 to 1.4	7,400	2,023	55	36	7,455	2,059
1.4 to 3.5	2,070	2,454	55	52	2,125	2,506
3.5 to 6.9	1,955	3,985	45	69	2,000	4,054
6.9 to 10.3	980	4,199	35	194	1,015	4,393
10.3 to 20.7	1,475	11,048	305	702	1,780	11,750
20.7 to 34.5	600	7,414	140	578	740	7,992
34.5 to 51.7	165	3,913	20	73	185	3,986
51.7 to 69.0	90	3,146	0	0	90	3,146
69.0 to 103.4	80	6,940	15	147	95	7,087
Total	14,815	45,122	670	1,851	15,485	46,973

[a] Includes only tanks with capacity greater than 4.0 m^3.

[b] See ref 15.

[c] Calculated from equations detailed in this section (III.B).

[d] Floating-roof tanks are actually control devices and therefore have no uncontrolled VOC emissions.

[e] Emissions from pressure vessels assumed to be negligible.

Large fixed-roof storage tanks——more than 1900 m^3——are the source of an estimated 39% (17,580 Mg/yr) of the total uncontrolled fixed-roof-storage VOC emissions, although they comprise only 5.5% of the total number of tanks. Although smaller fixed-roof storage tanks——less than 75 m^3——constitute 50% of the total industry tankage, they contribute only 12% (5343 Mg/yr) of the emissions (see Table III-1).

Approximately 60% (26,650 Mg/yr) of the total VOC emissions is from the storage of materials having vapor pressures between 3.5 and 34.5 kPa. Materials stored in fixed-roof tanks and having vapor pressures higher than 34.5 kPa contribute 30% (14,000 Mg/yr) of the total estimated uncontrolled VOC emissions, and materials with vapor pressures of less than 3.5 kPa, although comprising 53% of the total volume stored, contribute only 10% (4470 Mg/yr) of the total estimated VOC emissions from fixed-roof storage (see Table III-2).

Pressure tanks are not a significant source of VOC emissions under normal operating conditions.

b. Loading and Handling[14,16]

Uncontrolled VOC emissions from loading are calculated to be 5848 Mg/yr and from transit to be 1727 Mg/yr, for a total of 7575 Mg/yr (see Table III-3).

Rail and truck shipments account for 83% (4874 Mg/yr) of the uncontrolled loading VOC emissions. Shipments of materials whose vapor pressures range from 6.9 to 34.5 kPa contribute 66% of the total uncontrolled VOC emissions for the industry.

Approximately 15% (5250 X 10^3 m^3) of the VOC shipments listed in Table II-3 (above 103.4 kPa vapor pressure) are considered to be stored and loaded in closed systems with negligible loss of VOC.

2. Present Industry Emissions (1977)

a. Storage Tanks——Current emissions from fixed-roof tanks for the SOCMI are estimated to be 29,562 Mg/yr and for floating-roof tanks to be 1851 Mg/yr, for a projected total of 31,413 Mg/yr. This is approximately 34% less than the

Table III-3. 1977 Loading and Transportation VOC Emissions by Material Vapor Pressure[a]
(Assuming No Control)

Vapor Pressure (kPa)	Annual Volume Shipped (10^3 m^3/yr)	Loading Loss (Mg/yr)[b]	Transportation Loss (Mg/yr)[b]	Total VOC Emissions (Mg/yr)[b]
0.001 to 1.4	8,743	174	31	205
1.4 to 3.5	3,429	240	43	283
3.5 to 6.9	3,543	440	96	536
6.9 to 10.3	3,111	581	141	722
10.3 to 20.7	6,866	2,052	559	2,611
20.7 to 34.5	3,043	1,213	440	1,653
34.5 to 51.7	530	330	120	450
51.7 to 69.0	454	396	144	540
69.0 to 103.4	424	422	153	575
Total	30,143	5,848	1,727	7,575

[a] See refs 14 and 16.

[b] Calculated from equations detailed in this section (III.B).

calculated uncontrolled emission levels. Tables III-4 and III-5 show the distribution of the estimated emissions by tank capacity and vapor pressure, respectively.

An estimated 2148 fixed-roof tanks have add-on controls. This represents about 15% of the total number of fixed-roof tanks in the industry.

Large tanks, above 950 m^3, account for about 41% of the total number of fixed-roof tanks with add-on controls.

Approximately 40% of the fixed-roof tanks containing material with a vapor pressure of 10.3 kPa or greater have add-on control devices.

Approximately 80% of the emissions from floating-roof tanks are from materials having a vapor pressure of between 6.9 and 34.5 kPa. These materials are usually stored in large tanks, with 72% of the floating-roof tank emissions coming from tanks larger than 1890 m^3.

As stated in Sect. III-C-1, pressure tanks are not a significant source of VOC emissions under normal operating conditions.

b. Loading and Handling——Current VOC emissions from loading are estimated to be 4830 Mg/yr and from transit to be 86 Mg/yr, for a total of 4917 Mg/yr (see Table III-6). This is a 35% reduction from the uncontrolled-emission levels. The major cause for reduction is the use of pressurized cargo carriers, estimated to be used at least 95% of the time, that have no VOC emissions during transport.

As stated in Sect. C-1, approximately 15% of the VOC shipments are considered to be stored and loaded in closed systems with negligible loss of VOC since the materials have vapor pressures equal to or greater than atmospheric pressure.

c. Miscellaneous——It is recognized that there are other sources of VOC emissions related to storage and handling of SOCMI materials. They include tank and cargo carrier clean-outs, spills from both loading and unloading operations,

Table III-4. Current 1977 Storage-Tank VOC Emissions by Tank Size and Type[a] (with Controls)

Tank Size[b] (m^3)	Fixed-Roof Tanks No. of Tanks	Fixed-Roof Tanks No. Controlled	Fixed-Roof Tanks Emissions[c] (Mg/yr)	Floating-Roof Tanks[d] No. of Tanks	Floating-Roof Tanks[d] Emissions[c] (Mg/yr)	Total[e] No. of Tanks	Total[e] No. Controlled	Total[e] Emissions[c] (Mg/yr)
4 to 40	4,495	339	1,731	0	0	4,495	339	1,731
40 to 75	2,825	310	1,988	10	7	2,750	320	1,995
75 to 115	1,425	154	1,189	0	0	1,360	154	1,189
115 to 150	550	53	1,304	15	7	625	68	1,311
150 to 190	800	39	757	25	15	915	64	772
190 to 380	1,375	161	2,742	85	209	1,460	246	2,951
380 to 950	1,560	215	4,000	140	157	1,700	355	4,157
950 to 1900	975	382	5,106	95	131	1,070	477	5,237
1900 to 3800	520	300	5,542	125	417	645	425	5,959
>3800	290	195	5,203	175	908	465	370	6,111
Total	14,815	2,148	29,562	670	1,851	15,485	2,818	31,413

[a] Includes only tanks with capacity greater than 4.0 m^3.

[b] See ref 15.

[c] Determined by estimating the add-on controls in use and applying to the uncontrolled emissions at 80% control efficiency.

[d] Floating-roof tanks are actually control devices and therefore have no uncontrolled VOC emissions.

[e] Emissions from pressure vessels assumed to be negligible.

Table III-5. Current 1977 Storage-Tank VOC Emissions by Material Vapor Pressure and Tank Type[a] (with Controls)

Vapor Pressure[b] (kPa)	Fixed-Roof Tanks			Floating-Roof Tanks[d]		Total[e]		
	No. of Tanks	No. Controlled	Emissions[c] (Mg/yr)	No. of Tanks	Emissions[c] (Mg/yr)	No. of Tanks	No. Controlled	Emissions[c] (Mg/yr)
0.001 to 1.4	7,400	370	1,999	55	36	7,455	425	2,035
1.4 to 3.5	2,070	207	2,315	55	52	2,125	262	2,367
3.5 to 6.9	1,955	391	3,404	45	69	2,000	436	3,473
6.9 to 10.3	980	245	3,416	35	194	1,015	280	3,610
10.3 to 20.7	1,475	443	8,450	305	702	1,780	748	9,152
20.7 to 34.5	600	240	5,099	140	578	740	380	5,677
34.5 to 51.7	165	99	2,092	20	73	185	119	2,165
51.7 to 69.0	90	77	1,064	0	0	90	77	1,064
69.0 to 103.4	80	76	1,723	15	147	95	91	1,870
Total	14,815	2,148	29,562	670	1,851	15,485	2,818	31,413

[a] Includes only tanks with capacity greater than 4.0 m^3.

[b] See ref 15.

[c] Determined by estimating the add-on controls in use and applying to the uncontrolled emissions at 80% control efficiency.

[d] Floating-roof tanks are actually control devices and therefore have no uncontrolled VOC emissions.

[e] Emissions from pressure vessels assumed to be negligible.

Table III-6. Current 1977 Loading and Transportation VOC Emissions by Material Vapor Pressure[a] (with Controls)

Vapor Pressure (kPa)	Annual Volume Shipped (X 10^3 m^3/yr)	Loading Loss (Mg/yr)[b]	Transportation Loss (Mg/yr)[c]	Total VOC Emissions (Mg/yr)[b]
0.001 to 1.4	8,743	174	1	175
1.4 to 3.5	3,429	230	2	232
3.5 to 6.9	3,543	405	5	410
6.9 to 10.3	3,111	525	7	532
10.3 to 20.7	6,866	1,806	28	1,834
20.7 to 34.5	3,043	1,019	22	1,041
34.5 to 51.7	530	264	6	270
51.7 to 69.0	454	238	7	245
69.0 to 103.4	424	169	8	177
Total	30,143	4,830	86	4,917

[a] See refs 14 and 16.

[b] Determined by estimating the add-on controls used and applying them to the uncontrolled emissions at 80% control efficiency.

[c] Transportation loss estimated to be 5% or less of uncontrolled loss due to use of pressurized cargo carriers.

losses from breaking of hose and coupling connections, purging of tanks and cargo carriers to eliminate explosive mixtures, etc. These emissions are not controlled and have not been estimated because they are believed to be small compared to the total VOC emissions lost from storage tanks and loading operations.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. CONTROL TECHNOLOGY

There are several different methods, with varying ranges of efficiency, for the control of emissions from the storage and handling of organic chemicals.

A. STORAGE TANKS

1. Emission Control Techniques

Fixed-roof tanks represent minimal control technology. They are inadequate for storing the more volatile organic compounds, as is demonstrated by the high emission levels presented in Sect. III. Emissions are significant even with vapor pressures as low as 3.4 kPa.

a. Internal Floating Roofs in Fixed-Roof Tanks——Fixed-roof tank emissions can be reduced by installing internal floating roofs and seals in the tanks to minimize evaporation of the product being stored. Three floating-roof and seal combinations have been tested for use in fixed-roof tanks, including a noncontact internal floating roof with shingled, vapor-mounted, primary and secondary seals; a contact internal floating roof with a liquid-mounted primary seal; and a contact internal floating roof with a liquid-mounted primary seal and a continuous secondary seal. Based on the test results a noncontact internal floating roof with shingled, vapor-mounted, primary and secondary seals is not as effective in reducing emissions as a contact internal floating roof with a liquid-mounted primary seal.[1] Consequently, a larger emissions reduction can be achieved by fitting a fixed-roof tank with a contact internal floating roof and a liquid-mounted primary seal rather than with a noncontact internal floating roof and shingled, vapor-mounted, primary and secondary seals. Installation of a continuous secondary seal on a contact internal floating roof yields even more emissions reduction.

Several other roof and seal combinations, which have not been tested, are also available for controlling the emissions from fixed-roof tanks. Some of these include (1) a noncontact internal floating roof with a vapor-mounted primary seal; (2) a contact internal floating roof with a vapor-mounted primary seal; and (3) a contact internal floating roof with a vapor-mounted primary seal and a continuous secondary seal. Based on engineering judgment, a noncontact roof with a vapor-mounted primary seal would be less effective in reducing emissions than the noncontact roof tested, which was equipped with both primary and secondary seals. In addition, information presented in American Petroleum Institute (API) Bulletin 2517[2] regarding the effectiveness of liquid-mounted and vapor-mounted primary seals on external floating roofs indicates that the contact internal floating and liquid-mounted primary seal tested would be more effective at reducing emissions than a contact roof with a vapor-mounted primary seal. As was also indicated in the test of a contact internal floating roof, a secondary seal over a vapor-mounted primary seal may be expected to result in even larger emissions reduction.

b. Rim-Mounted Secondary Seals on External Floating Roofs——A rim-mounted secondary seal on an external floating roof is a continuous seal that extends from the floating roof to the tank wall, covering the entire primary seal. Installed over a mechanical shoe seal, this secondary seal has been demonstrated to effectively control VOC emissions that escape from the small vapor space between the shoe and the wall or through any openings or tears in the seal envelope (see Fig. IV-1a). Rim-mounted secondary seals should also be effective in controlling emissions from the liquid- and vapor-mounted primary seals shown in Figs IV-1b, IV-1c, and IV-1d.[3]

Another type of secondary seal, which has not been tested, is a shoe-mounted secondary seal. A shoe-mounted seal extends from the top of the shoe to the tank wall (see Fig. IV-2).[3] These seals do not provide protection against VOC leakage through the envelope. Holes, gaps, tears, or other defects in the envelope can allow direct communication between the saturated vapor under the envelope and the atmosphere; the wind can enter this space through envelope defects, flow around the circumference, and exit with saturated or nearly saturated VOC vapors.

c. Fixed Roofs on External Floating Roof Tanks——Installing a fixed-roof on an existing external-floating-roof tank would reduce emissions by reducing the effect of wind sweeping vapors out of the vapor space and into the atmosphere.

An alternative to the construction of a new external-floating-roof tank is the construction of an internal-floating-roof tank with a primary seal or both primary and secondary seals.

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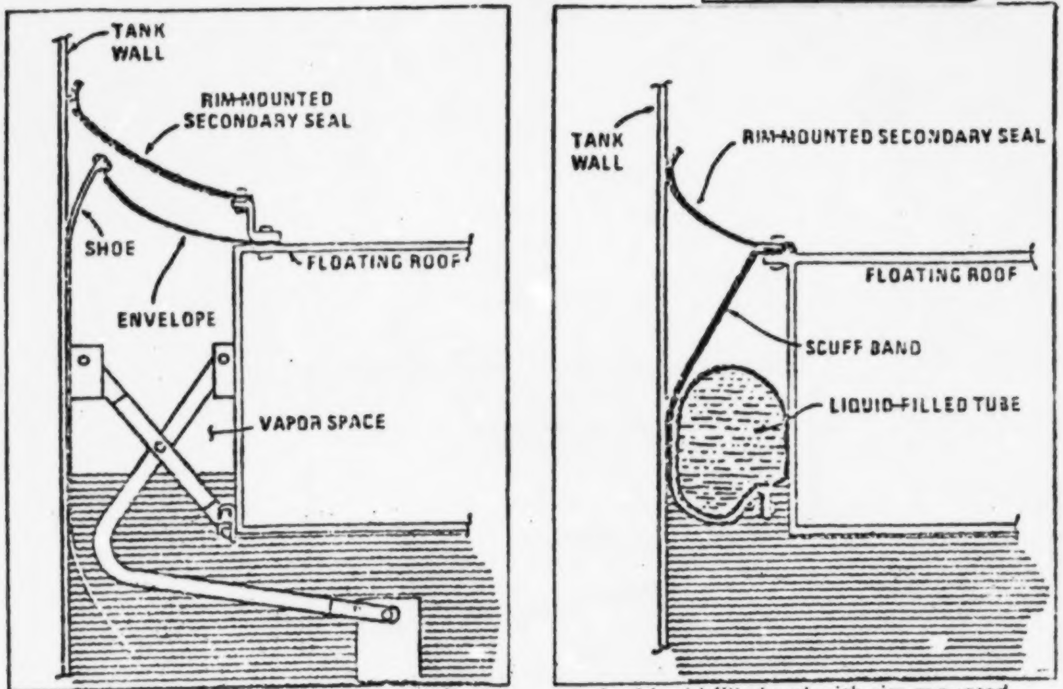
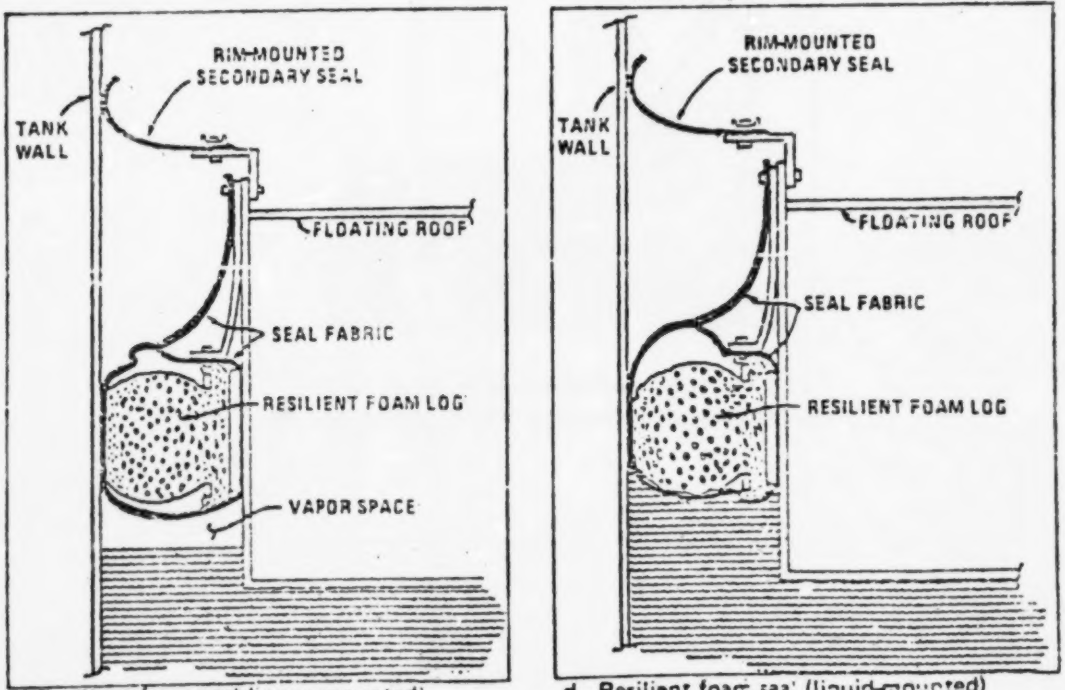


a. Shoe seal with rim-mounted secondary seal.

b. Liquid-filled seal with rim-mounted secondary seal.



c. Resilient foam seal (vapor-mounted) with rim-mounted secondary seal

d. Resilient foam seal (liquid-mounted) with-rim-mounted secondary seal

Fig. IV-1. Rim-mounted Secondary Seals on External Floating Roofs (from ref 3).

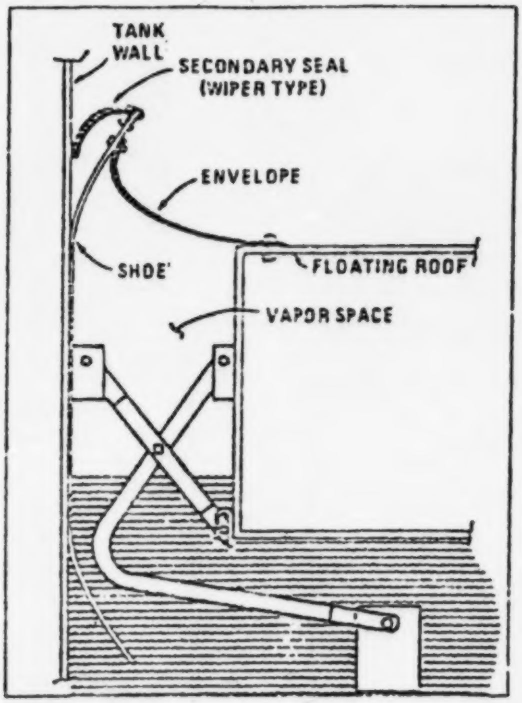


Fig. IV-2. Metallic Shoe Seal with Shoe-Mounted Secondary Seal (from ref 3)

d. Rim-Mounted Secondary Seals on Noncontact Internal Floating Roofs—Because there are some noncontact internal-floating-roof tanks that have only vapor-mounted primary seals, another control technique is to install rim-mounted secondary seals over the primary seals. This seal, which is typically a wiper seal, minimizes the effects from air currents inside the tank sweeping vapors out of the annular vapor space. This type of seal can be either continuous or shingled and extends from the floating roof to the tank wall, covering the primary seal. Although the benefit of using a secondary seal cannot be quantified because a noncontact roof with only a vapor-mounted primary seal has not been tested, engineering judgment indicates that this modification would reduce the emissions from noncontact internal-floating-roof tanks.

e. Contact Internal Floating Roofs in Noncontact Internal-Floating-Roof Tanks—Recent pilot test tank studies sponsored by EPA have demonstrated that noncontact internal-floating-roofs with shingled, vapor-mounted, primary and secondary seals may not be as effective in reducing emissions as contact internal floating roofs with liquid-mounted primary seals.[1] Based on these studies one emission control technique for internal-floating-roof tanks is the use of contact internal floating roofs with liquid-mounted primary seals instead of noncontact internal floating roofs with shingled, vapor-mounted, primary and secondary seals. The use of a continuous secondary seal on the contact internal-floating-roof has been demonstrated to result in an even larger emission reduction.

Two roof and seal combinations, which have not been demonstrated, are a contact internal-floating-roof with a vapor-mounted primary seal and a contact internal-floating-roof with vapor-mounted primary and secondary seals. Engineering judgment indicates that the use of either of these roof and seal combinations would result in lower emissions than those associated with the use of a noncontact roof with a vapor-mounted primary seal or vapor-mounted primary and secondary seals.

f. Liquid-Mounted Primary Seals on Contact Internal Floating Roofs—Based on information reported in API Bulletin 2517[2] and engineering judgment, vapor-mounted primary seals are not as effective in reducing emissions as liquid-mounted primary seals. As a result one technique to reduce the emissions from tanks having contact internal floating roofs is the use of liquid-mounted rather than vapor-mounted primary seals.

g. Rim-Mounted Secondary Seals on Contact Internal Floating Roofs——Contact internal floating roofs, like other types of floating roofs, can have not only a primary seal to cover the annular vapor space but also a rim-mounted secondary seal (Fig. IV-3).[1] This secondary seal, which is typically a wiper seal or a resilient foam-filled seal, minimizes the effects from the air currents inside the tank sweeping vapors out of the annular vapor space. This type of seal is continuous and extends from the floating roof to the tank wall, covering the entire primary seal.

h. Carbon Adsorption—Carbon adsorption utilizes the principle of carbon's affinity for nonpolar hydrocarbons to remove VOC from the vapor phase. Activated carbon is the adsorbent and the VOC vapor that will be removed from the air stream is referred to as the adsorbate. Adsorption of the VOC vapor occurs at the surface of the adsorbent and is a physical process since no chemical change takes place. The VOC carbon adsorption unit consists of a minimum of two carbon beds plus a regeneration system. Two or more beds are necessary to assure that one bed will be available for use while the other one is being regenerated.

Regeneration can be performed with either steam or vacuum (Fig. IV-4).[4] In steam regeneration, steam is circulated through the bed, raising the VOC vapor pressure. The vaporized VOC is thus removed along with the steam. The steam-VOC mixture is condensed, ususally by an indirect cooling-water stream, and routed to a separator. The VOC is then decanted and returned to storage, and the contaminated water is sent to the plant wastewater system for disposal. Cooling water, electricity, and steam are the required utilities for a steam regeneration system. The other method of regenerating the carbon, vacuum regeneration, consists of a high vacuum being pulled on the carbon bed. The VOC vapor desorbed by this process is condensed and returned to storage.

The size of the carbon adsorption units depends on the type and concentrations of the VOC components in the vent gas, on the gas flow rate, and on the time required for regeneration.

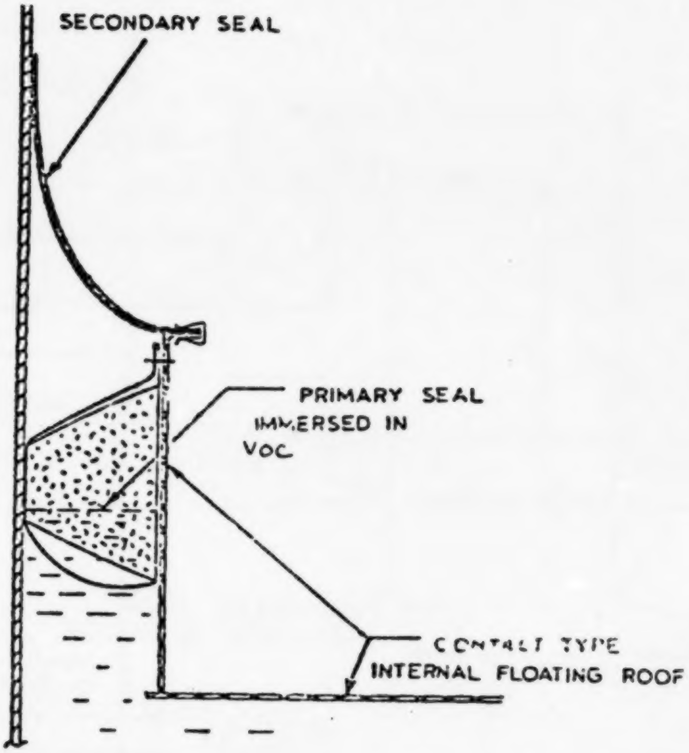

SECONDARY SEAL
PRIMARY SEAL IMMERSED IN VOC
CONTACT TYPE INTERNAL FLOATING ROOF

Fig. IV-3. Rim Mounting of a Secondary Seal on an Internal Floating Roof (from ref 1)

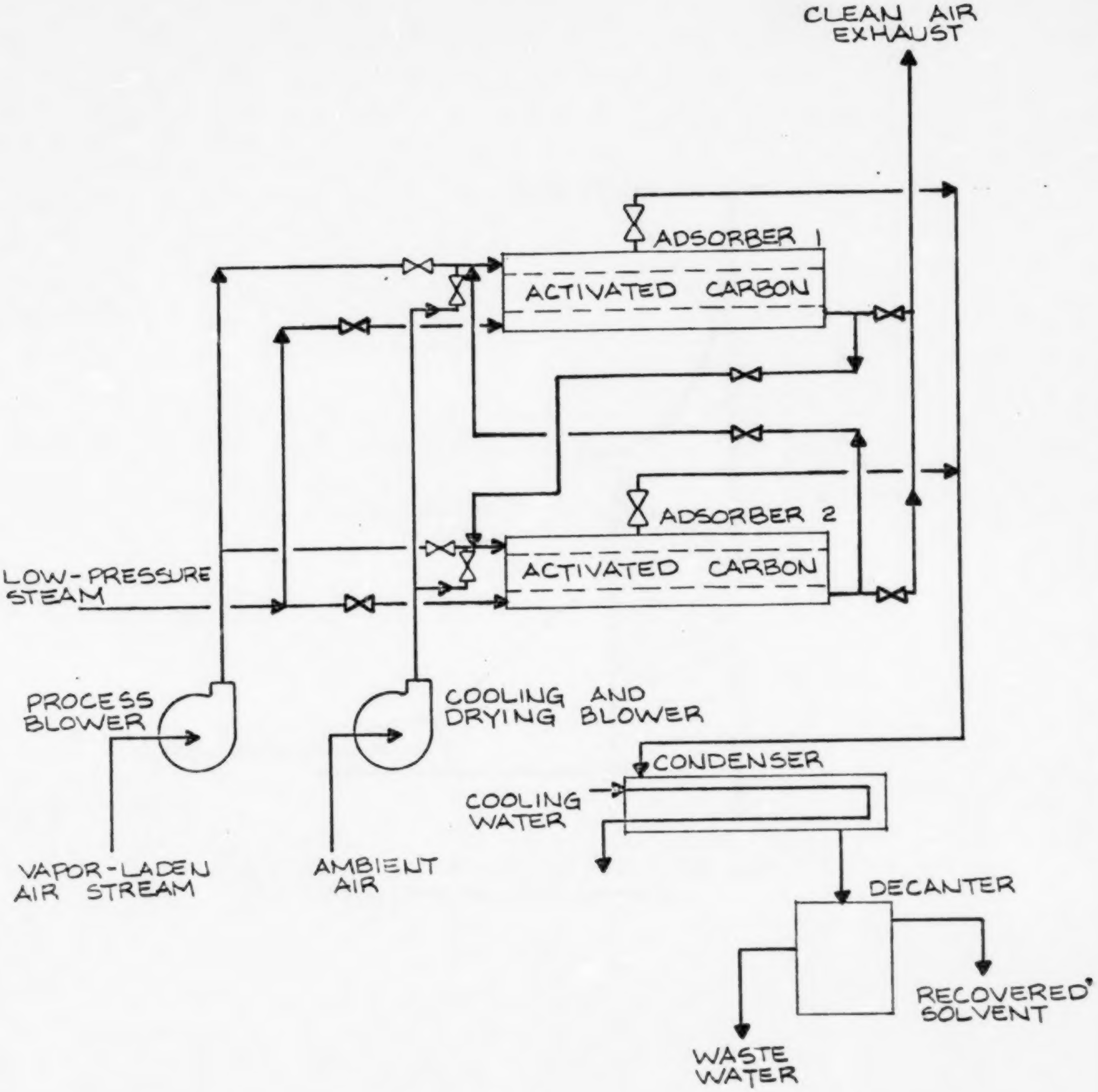


Fig. IV-4. Activated-Carbon Adsorption System (from ref 4)

i. Thermal Oxidation——In a typical thermal oxidation system the air-vapor mixture is injected via a burner manifold into the combustion area of the incinerator. Pilot burners provide the ignition source and supplementally fueled burners add heat when the flame temperature is required to be maintained between 1030 K and 1090 K (1400°F and 1500°F).

The amount of combustion air needed is regulated by temperature-controlled dampers. The concentration of VOC in the tail gas of an oxidizer can be limited to 10 ppm.[5] Figure IV-5[5] shows a typical thermal oxidation unit.

Flashback prevention and burner stability are achieved by saturating the VOC vapors to a concentration above the upper explosive limit. In addition two water-seal flame arrestors are used to assure that flashbacks do not propagate from the burner to the rest of the piping system.

A significant advantage of thermal oxidizers is that they can dispose of a wide range of hydrocarbons. This is especially important at a tank farm where numerous hydrocarbon liquids are stored.

Normally, thermal oxidation as a control for storage-tank VOC emissions cannot be justified economically unless it is combined with a more significant process-vent emission control system.

j. Refrigerated Vent Condensers——Refrigerated vent condensers for controlling fixed-roof storage-tank VOC emissions are one of the most common types of emission reducion equipment found in the industry.[6]

Condensers are sized to handle the maximum vapor rate expected at any given time, which normally occurs during the tank filling operation. In actual service one condenser can be used to collect the vapors from a manifold system of tanks containing the same material.

The refrigerated condenser must be properly designed to handle freezing of moisture or VOC. This is accomplished by a system that routinely defrosts the condenser and then separates the recovered water-VOC mixture. Package units are available in a range of sizes for various applications.[7] An example of a refrigerated vent condenser is shown in Fig. IV-6.[8]

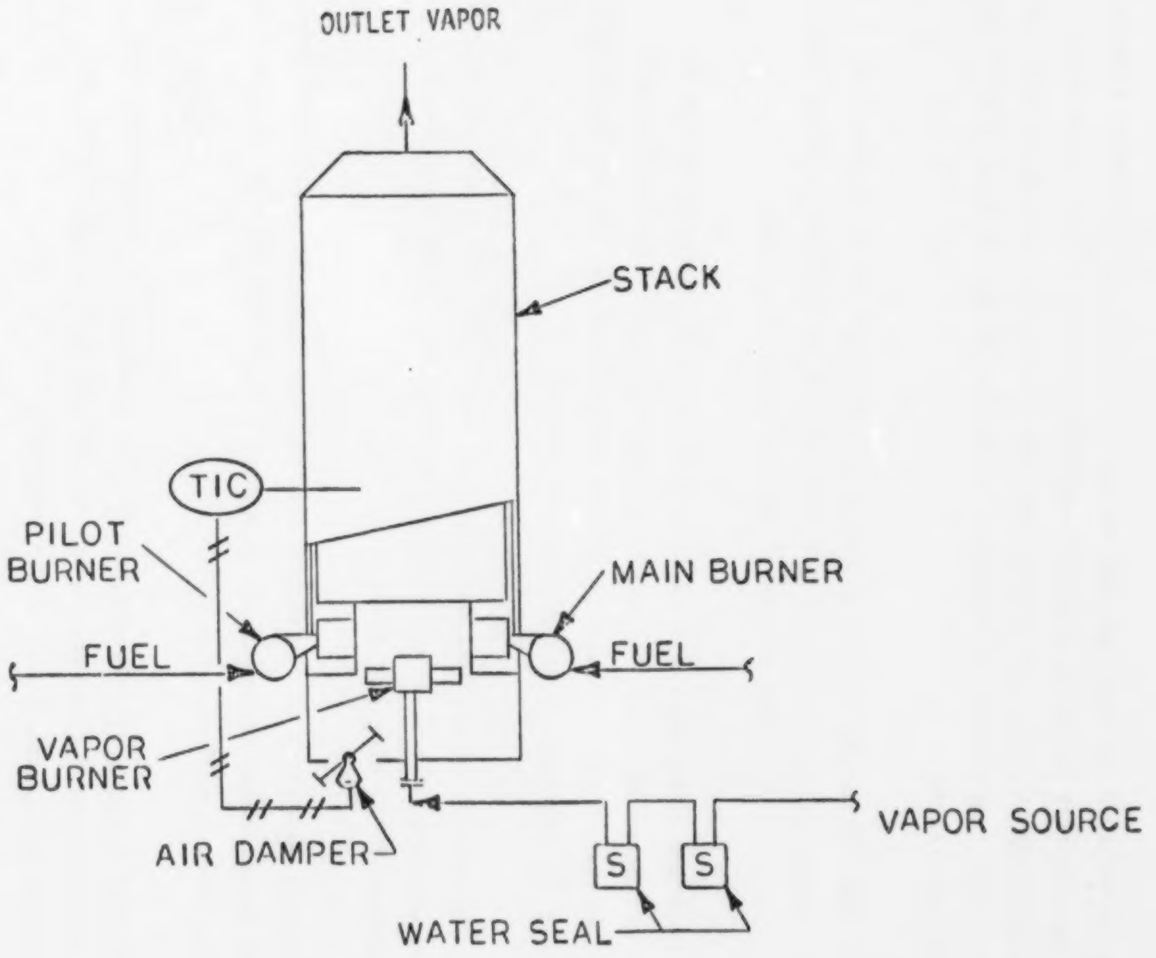


Fig. IV-5. Thermal Oxidation Unit (from ref 5)

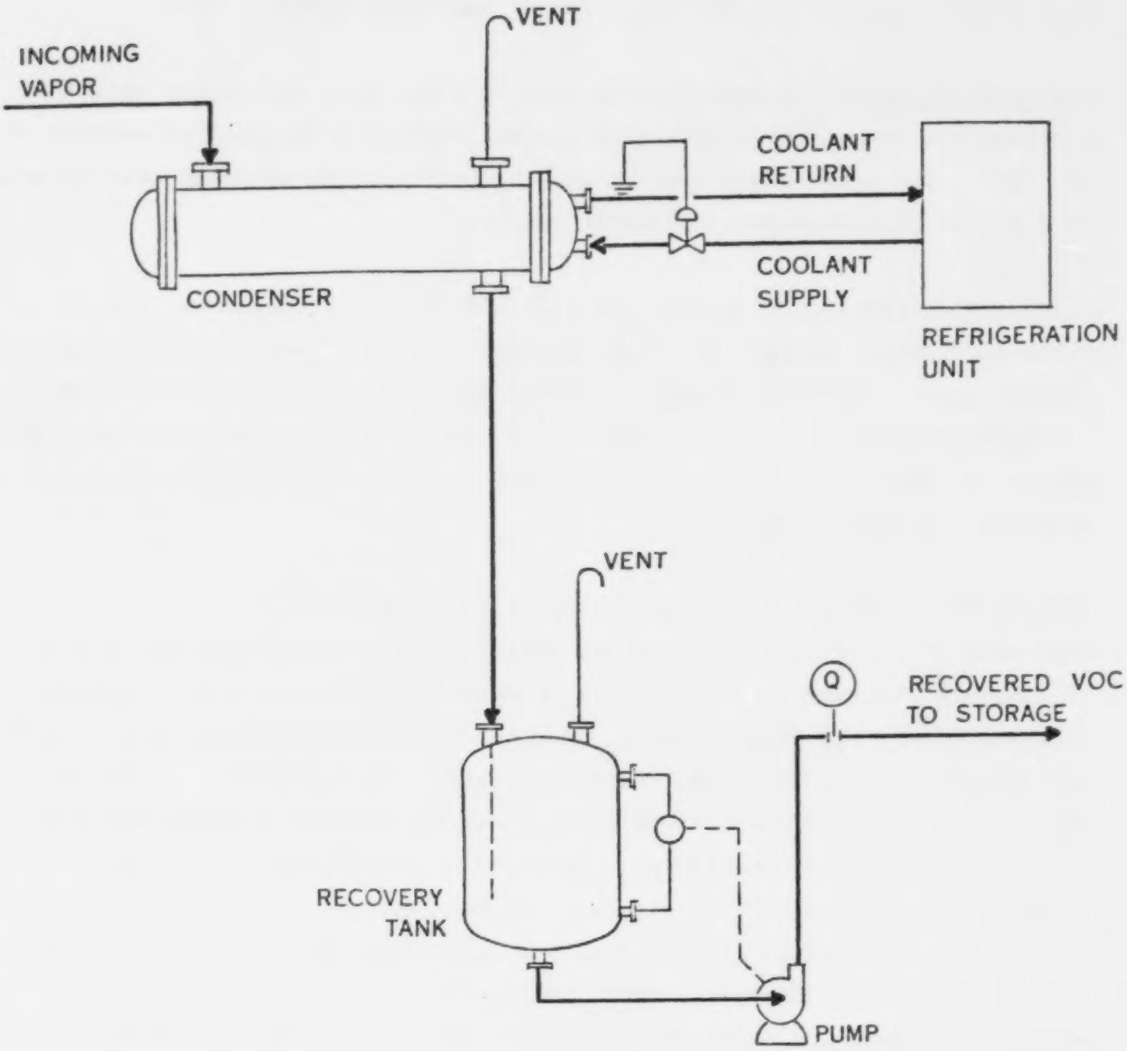


Fig. IV-6. Refrigerated Vent Condenser System

k. Pressure Vessels——Pressure vessels as described in Sect. II can be considered as a control alternative for small fixed-roof tanks (under 15 m^3).

1. Conservation Vents——A conservation vent is a pressure and vacuum vent that provides a large gas flow area with a small differential pressure setting of ±0.2 kPa. The seal is provided by gasketed plates held in place over an opening by a system of levers and adjustable weights.

Conservation vents will achieve low-cost VOC emission control for fixed-roof tanks that do not warrant the floating-roof or other types of control options covered above. Exceptions would be their application on fixed-roof tanks containing chemicals that could partly or completely plug the vents in a short period of time (i.e., shorter than a biannual inspection period) and result in structural damage to the tank.

2. Control Efficiencies of Emissions Control Techniques

This section establishes the typical control efficiencies expected with the use of external floating roofs with both primary and secondary seals, internal floating roofs with primary seals, internal floating roofs with both primary and secondary seals, and vapor control systems. The efficiencies are estimated for only those emissions control techniques that have been demonstrated to be effective in reducing emissions. Equations shown in Sect. III, which are based on AP-42 emissions equations and test results recently reported by the Western Oil and Gas Association (WOGA), EPA, and the German Society for Petroleum Science and Carbon Chemistry (DGMK), are used to estimate fixed-roof-tank emissions. Equations shown in Appendix B, which are based on testing conducted for EPA, are used in estimating the emissions from external-floating-roof tanks with primary seals; from external-floating-roof tanks with primary and secondary seals; from noncontact internal-floating-roof tanks with vapor-mounted primary and secondary seals; from contact internal-floating-roof tanks with liquid-mounted primary seals; and from contact internal-floating-roof tanks with both liquid-mounted primary seals and continuous secondary seals.

It is emphasized that the emissions equations are based on limited amounts of empirical data, and therefore should be used only to estimate, rather than to precisely predict, the emissions. In addition the efficiency for each emission control technique should be used only for making comparisons of the relative effectiveness of the control techniques.

a. Internal Floating Roofs in Fixed-Roof Tanks——If a noncontact internal floating roof with shingled, vapor-mounted, primary and secondary seals is installed in a fixed-roof tank 18 m in diameter, 12 m in height, and undergoing 13 turnovers per year, the annual VOC emissions are reduced from 21 Mg to 8.8 Mg, a 58% reduction. Installation of a contact internal floating roof with a liquid-mounted primary seal in the same fixed-roof tank reduces VOC emissions from 21 Mg/yr to 3.5 Mg/yr an 83% reduction. Installing a contact internal floating roof with a liquid-mounted primary seal and a continuous secondary seal in the fixed-roof tank will reduce the annual VOC emissions by 90% to 2.2 Mg.

b. Rim-Mounted Secondary Seals on External Floating Roofs——If the baseline is an 18-m-diam, 12-m-high external-floating-roof tank with 13 turnovers per year, the annual emissions are estimated to be about 18 Mg. If this tank has a secondary seal over the primary seal, annual emissions are about 13 Mg, a 28% reduction.

c. Fixed-Roofs on External-Floating-Roof Tanks——If a roof is installed on an existing external-floating-roof tank 18 m in diameter, 12 m high, with 13 turnovers per year, the tank has emissions of the same order of magnitude as a contact internal-floating-roof tank with a liquid-mounted primary seal. As a result the annual benzene emissions are about 3.5 Mg, which is an 81% reduction of the 18 Mg/yr emitted from the external-floating-roof tank. If the same tank is retrofitted with a secondary seal and a fixed roof, the annual emissions are reduced by 88%, or to 2.2 Mg.

If a new external-floating-roof tank with both primary and secondary seals is the baseline, the construction of a contact internal-floating-roof tank with a liquid-mounted primary seal would reduce annual emissions to 3.5 Mg. This amount is a 73% reduction from the baseline emissions of 13 Mg/yr. An 83% reduction equivalent to annual emissions of 2.2 Mg would be achieved with construction of a contact internal-floating-roof tank with both primary and secondary seals.

Another alternative to the construction of a new external-floating-roof tank is a noncontact internal floating-roof tank. With an external-floating-roof tank with a primary seal used as the baseline, this control option results in a 51% reduction of the annual emissions, or from 18 to 8.8 Mg. If a new external-floating-roof tank with both primary and secondary seals is the baseline, the annual emissions are reduced from 13 Mg to 8.8 Mg, a 32% reduction.

d. Contact Internal Floating Roofs in Noncontact Internal Floating-Roof Tanks——Installing a contact internal floating roof with a liquid-mounted primary seal in a noncontact internal-floating-roof tank 18 m in diameter, 12 m high, and undergoing 13 turnovers per year reduces the annual VOC emissions to 3.5 Mg. This amount is a 60% reduction from the 8.8 Mg/yr emitted from the noncontact internal-floating-roof tank.

If a contact internal floating roof with a liquid-mounted primary seal and a continuous secondary seal is installed in a noncontact internal-floating-roof tank, the annual emissions are reduced by 75%, or to 2.2 Mg.

e. Rim-Mounted Secondary Seals on Contact Internal Floating Roofs——Installation of a secondary seal on an 18-m-diam, 12-m-high contact internal-floating-roof tank with 13 turnovers per year reduces the annual VOC emissions from 3.5 Mg to 2.2 Mg, which is a 37% reduction in emissions.

f. Carbon Adsorption——The carbon-adsorption vapor control system is estimated to reduce the storage-tank emissions by approximately 96%. This efficicncy is based on a measured carbon-adsorption unit efficiency of 98% during gasoline loading operations[4] and an assumed collection efficiency of 98% of the VOC emissions.

If a carbon-adsorption system with this efficiency is used on a fixed-roof tank 18 m in diameter, 12 m in height, and undergoing 13 turnovers per year, the VOC emissions are reduced from 21 Mg/yr to 0.89 Mg/yr, a 96% reduction.

Because the emissions from the carbon-adsorption unit are directly related to the volume of saturated vapor entering the unit, the use of an internal floating roof in the same fixed-roof tank does not reduce the overall emissions. Consequently the emissions from a carbon-adsorption unit that is fitted to a noncontact or a contact internal-floating-roof tank remain unchanged at 0.89 Mg/yr. However, because the annual emissions from these internal-floating-roof tanks are only 8.8 Mg and 3.5 Mg, the emission reduction efficiencies from the use of a carbon-adsorption system are only 90 and 75% respectively. These efficiencies are lower than the 96% efficiency expected, because the vapor emitted from each tank is saturated with VOC for safety reasons before its introduction to the carbon-adsorption unit. Consequently the emission reductions achieved by the carbon adsorber are based on the VOC concentration leaving the saturator and not on the concentration from the storage tank.

In order to use a carbon-adsorption system on an external-floating-roof tank, a fixed roof with pressure-vacuum vents must be installed over the floating roof.

g. Thermal Oxidation——The thermal-oxidation vapor control system is estimated to reduce the VOC emissions by approximately 97%. This efficiency is based on a measured thermal-oxidation-unit efficiency of 99% during gasoline-loading operations[9] and an assumed 98% collection efficiency of the emissions.

Connecting a thermal-oxidation system of 97% efficiency to a fixed-roof tank 18 m in diameter, 12 m high, and undergoing 13 turnovers per year reduces benzene emissions from 22 Mg/yr to about 0.67 Mg/yr, a 97% reduction.

If a thermal-oxidation system is used on a noncontract internal-floating-roof tank, the emissions are reduced from 8.8 Mg/yr to 0.67 Mg/yr, a 92% reduction. As with carbon adsorption, the percentage of emissions reduced can be less than the overall control efficiency indicated, because the vapors may have to be saturated.

The use of this system on a contact internal-floating-roof tank reduces emissions from 3.5 Mg/yr to 0.67 Mg/yr, an 81% reduction.

Before a thermal oxidation system can be used on an external-floating-roof tank, the tank must be modified by the installation of a fixed roof with pressure-vacuum vents over the floating roof.

h. Refrigerated Vent Condenser—The efficiency of vent condensers depends on the vapor concentration of the VOC in the vent gas and on the condensing temperature. Normally the VOC partial pressure in the effluent gas streams can be reduced to 3.4 to 0.7 kPa.[7] Theoretical recovery efficiencies can be in excess of 90% for VOC whose vapor pressures are over 34.5 kPa, and 60 to 90% for materials with vapor pressures in the range of 3.4 to 34.5 kPa.

i. Pressure Vessels—Under normal conditions no VOC losses will be experienced from pressure vessels. If an inert-gas pad is used for safety or operating reasons, losses will be similar to those experienced from variable vapor-space tanks (i.e., reductions of 98% in VOC emissions from a fixed-roof tank).[10]

j. Conservation Vents—The use of a conservation vent reduces the amount of breathing losses from fixed-roof tanks by venting only when the design pressure differential is exceeded. Estimated emission control efficiencies of tank breathing losses range from 5 to 25%+, depending on the vapor pressure of the material stored.[11]

The effectiveness of any of the control devices described above will be reduced significantly if a proper maintenance and inspection program is not followed. A biannual inspection program with followup repairs is suggested for all control devices, including seals on floating roofs, to ensure maximum control of VOC emissions from storage tanks, regardless of the type.

3. Retrofitting Problems

This section covers possible problems that fixed-roof-tank owners and operators may have in retrofitting their tanks with internal floating roofs. In addition problems associated with the retrofitting of rim-mounted secondary seals on external floating roofs, conversion of external-floating-roof tanks to internal-floating-roof tanks and the retrofitting of vapor control systems to tanks are discussed.

a. Fixed Roof Tanks with Internal Floating Roofs—Several modifications may be necessary on a fixed-roof tank before it can be equipped with an internal floating roof. Tank shell deformations and obstructions may require correction, and special structural modifications such as bracing, reinforcing, and plumbing vertical columns may be necessary. Antirotational guides should be installed to keep cover openings in alignment with roof openings. Special vents must be installed on the fixed roof or on the walls at the top of the shell to minimize the possibility of VOC vapors approaching the flammable range in the vapor space.

b. Rim-Mounted Secondary Seals on External Floating Roofs——Retrofitting problems may be encountered when a secondary seal is installed above a primary seal, which can accommodate a large amount of gap. Some secondary seals may not be able to span as large a gap, and consequently excessive gaps may result between the secondary seal and the tank shell.

c. Fixed Roofs on External Floating Roof Tanks——In order to install a fixed roof on an existing external-floating-roof tank, several tank modifications may be required. For example, special structural modifications such as bracing and reinforcing may be necessary to permit the external-floating-roof tank to accommodate the added weight of a fixed roof. Vertical columns may be required to support the fixed roof, and as a result modifications to the floating roof will be necessary to accommodate these columns. In addition antirotational guides should be installed to keep cover openings in alignment with roof openings.

d. Carbon Adsorption——If a carbon-adsorption system is employed for reducing emissions, steam can be used for regeneration of the carbon beds. However, a source of steam may not be readily available at some facilities. In addition water for cooling may also be in short supply. Furthermore, even if cooling water is available, disposal of VOC-contaminated condensate could be a problem. If water for cooling is not easily obtained or if steam is not readily available, a vacuum regeneration system with a closed-loop freon refrigeration unit can be used to regenerate the carbon. This method would also eliminate the problem of disposal of VOC-contaminated water.

e. Thermal Oxidation——The biggest problem with the use of thermal oxidation is the requirement for supplemental fuel to maintain the flame temperature. Some facilities may not have adequate fuel supplies readily available.

B. LOADING AND HANDLING

Loading emissions can be controlled by any of the methods described below.

1. Submerged Loading

The princinpal methods of loading cargo carriers are splash loading and sub-merged loading. The two types of submerged loading are the submerged-fillpipe and the bottom-loading methods. In the submerged-fillpipe method the fillpipe descends almost to the bottom of the cargo tank. In the bottom-loading method the material enters the cargo tank from the bottom. Submerged loading significantly reduces liquid turbulence and vapor-liquid contact and results in much lower VOC losses than are experienced with splash loading. Emission reductions can range from 0 to 65%, depending on the method used by the cargo carrier.[12]

2. Vapor Recovery

Vapor recovery equipment recovers the VOC vapors displaced during loading and ballasting operations by use of refrigeration, adsorption, and/or absorption, as described above for fixed-roof tanks. Control efficiencies range from 90 to 95%, depending on the nature of the VOC emissions and the type of recovery equipment used.[12]

3. Vapor Oxidation

Vapor oxidation with thermal-oxidation devices can give greater than 97-99+% VOC emissions control. As an example, in the petroleum industry gasoline vapors from a terminal are displaced to a vapor holder as they are generated. When the gasoline vapors reach satuaration in the holder, they are released to the oxidizer, after being mixed with a properly metered air stream, and are then combusted. The thermal oxidizer is not a true afterburner; rather, it operates in the manner of an enclosed flare.[13]

Twelve to fifteen thermal oxidizers have reportedly been installed by gasoline terminal operators. Later models of this type of control equipment do not require vapor holders; vapors from the tank trucks created during loading operations are vented directly to the thermal oxidizer.[13]

4. Vapor Balance

Another method of loading that can be used to reduce VOC emissions is called dedicated balance service. Cargo carriers in dedicated balance service pick up vapors displaced from the receiving tank during unloading operations and transport them in the empty cargo tanks back to the loading terminal.[12] These vapors can then be displaced, during subsequent refilling of the cargo carrier, to an emission control device installed at the loading terminal.

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13. Control of Hydrocarbons from Tank Truck Gasoline Loading Terminals, Guideline Series, EPA-450/2-77-026 (OAQPS No. 1.2-082), Research Triangle Park, NC (October 1977).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

V. IMPACT ANALYSIS

A. ENVIRONMENTAL AND ENERGY IMPACT

1. Storage Tanks

To assess the impacts of the various control options, models that are representative of the industry storage tanks were devised; see Table V-1 for the parameters used in the evaluation.

a. Fixed-Roof-Tank Emissions——The quantity of VOC emitted from a fixed-roof tank is primarily a function of the capacity of the tank itself and of the vapor pressure of the chemical stored in the tank. Table V-2 shows the VOC emissions in Mg/yr that would be expected for the nine selected model-tank sizes at seven selected vapor pressures.

The smallest tank selected was 40 m^3 and the largest was 8330 m^3. The vapor pressures selected ranged from 1.0 kPa to 51.7 kPa. VOC emissions increase with increasing tank size and increasing vapor pressure.

Emissions were calculated based on the fixed-roof breathing- and working-loss equations discussed in Sect. III of this report.

Internal floating roofs used on fixed-roof tanks (new and retrofitted) sources——Table V-3 shows the VOC emission reduction that can be achieved by fitting a contact internal floating roof with a liquid primary seal and a continuous secondary seal to a fixed-roof tank.

A control efficiency of 85% was used to calculate emission reductions, which represents the average control efficiency that could be expected for the range of tank sizes (40—8330 m^3) and vapor pressures (1.0—51.7 kPa) evaluated.

In operation, floating-roof storage tanks do not consume any raw materials or utilities and have no adverse environmental or energy impacts.

Table V-1. Model Parameters Used for Assessing Impacts of Industry Storage Tanks*

Model Tank Capacity (m^3)	Dimensions (m)		Turnovers Per Year
	Diameter	Height	
40	4.5	2.4	200
75	4.5	4.9	200
115	4.5	7.3	200
150	5.1	7.3	200
285	7.0	7.3	100
660	8.3	12.2	50
1420	12.2	12.2	36
2840	17.2	12.2	24
8330	29.5	12.2	12

*Average liquid density of materials controlled = 792 kg/m^3.

Table V-2. Uncontrolled VOC Emissions vs Absolute Vapor Pressures of Material Stored for Model Fixed-Roof Tanks*

Tank Capcity (m^3)	VOC Emissions (Mg/yr) for Vapor Pressures of						
	1.0 kPa	1.4 kPa	3.4 kPa	6.9 kPa	10.3 kPa	34.5 kPa	51.7 kPa
40	0.16	0.21	0.41	0.72	1.07	2.33	3.52
75	0.30	0.39	0.78	1.39	2.06	4.51	6.81
115	0.43	0.57	1.16	2.04	3.04	6.68	10.06
150	0.58	0.77	1.55	2.74	4.07	8.94	13.48
285	0.86	1.12	2.23	3.91	5.80	12.65	19.11
660	1.62	2.12	4.24	7.44	11.03	24.09	36.38
1420	3.24	4.25	8.50	14.92	22.12	48.34	72.99
2840	4.61	6.02	11.88	20.71	30.60	66.51	100.65
8330	7.92	10.25	19.65	33.66	49.33	105.85	160.99

*Calculated with equations discussed in Sect. III.

Table V-3. VOC Emission Reduction from Replacing Fixed-Roof Tanks with Internal-Floating-Roof Tanks vs Absolute Vapor Pressures of Materials

Model Tank Size (m^3)	VOC Emission Reduction (Mg/yr) for Vapor Pressures[a]						
	1.0 kPa (Mg/yr)	1.4 kPa (Mg/yr)	3.4 kPa (Mg/yr)	6.9 kPa (Mg/yr)	10.3 kPa (Mg/yr)	34.5 kPa (Mg/yr)	51.7 kPa (Mg/yr)
40	0.14	0.18	0.35	0.61	0.91	1.98	2.99
75	0.26	0.33	0.66	1.18	1.75	3.83	5.79
115	0.37	0.48	0.99	1.73	2.58	5.68	8.55
150	0.49	0.65	1.32	2.33	3.46	7.60	11.46
285	0.73	0.95	1.90	3.32	4.93	10.75	16.24
660	1.38	1.80	3.60	6.32	9.38	20.40	30.92
1420	2.75	3.61	7.23	12.68	18.80	41.09	62.04
2840	3.92	5.12	101.10	17.60	26.01	56.53	85.55
8330	6.73	8.71	16.70	28.61	41.93	89.97	136.84

[a] Using a control efficiency of 85%.

Refrigerated vent condenser (new and retrofitted sources)——Table V-4 shows the model parameters used for assessing the impacts from addition of a refrigerated vent condenser to a fixed-roof tank. Three model tank sizes (150, 660, and 2840 m^3), representing small, medium, and large SOCMI storage tanks respectively were selected for evaluation.

Three different cases representing three common conditions of condenser operation were selected for each of the model tanks and are also shown in Table V-4. For case 1 it was assumed that the chemical stored has a low vapor pressure, 3.5 kPa, and that the vapor pressure of the exit gas stream leaving the condenser has been reduced to 1.4 kPa. Case 2 is an evaluation of the storage of an average-vapor-pressure (10.3-kPa) chemical with a final (exit) vapor pressure of 1.4 kPa. For case 3 it was assumed that the chemical stored has a high vapor pressure, 51.7 kPa, and that the exit stream vapor pressure has been reduced to 3.5 kPa.

The physical properties of three different chemicals with vapor pressures nearly equal to the initial vapor pressures described for cases 1, 2, and 3 were averaged. These averages were used to calculate the size of each condenser and its accompanying refrigeration system. Sizing details are shown in Appendix B.

Table V-5 shows the VOC emissions expected from the three model fixed-roof tanks before and after a refrigerated vent condenser was added. Also included in the table is the amount of VOC reduced. Quantities are shown for all three cases of operation selected.

Refrigerated vent condensers do not consume any raw materials but do require electricity. The electrical requirements for each model tank selected are shown in Table V-6 as joules per gram of VOC recovered. Values range from 331 to 1854 J/g.

b. Floating-Roof-Tank Emissions——The quantity of VOC emitted from a floating-roof tank is primarily a function of the capacity (size) of the tank itself and of the vapor pressure of the chemical stored in the tank. Table V-7 shows the VOC emissions in Mg/yr that would be expected for the nine selected model tank sizes at five selected vapor pressures.

Table V-4. Model Parameters and Operating Conditions for Assessing Impacts from Refrigerated Vent Condensers

Fixed-Roof Tank Capacity (m^3)	Turnovers Per Year	Vapor Pressure (kPa) Initial	Vapor Pressure (kPa) Final	Final Temp. (°C)	Emission Reduction (%)
		Case 1			
150	200	3.5	1.4	10	60
660	50				
2840	24				
		Case 2			
150	200	10.3	1.4	-9.6	86.7
660	50				
2840	24				
		Case 3			
150	200	51.7	3.5	-20.3	93.3
660	50				
2840	24				

Table V-5. VOC Emissions from Fixed-Roof Tanks Before and After Refrigerated Condenser Add-on

Model Tank Capacity (m^3)	VOC Emissions (Mg/yr)								
	Before Add-On			After Add-On			Reduction		
	Case I	Case II	Case III	Case I	Case II	Case III	Case I	Case II	Case III
150	1.55	4.07	13.48	0.62	0.54	0.90	0.93	3.53	12.58
660	4.24	11.03	36.38	1.70	1.47	2.44	2.54	9.56	33.94
2840	11.88	30.60	100.65	4.75	4.07	6.74	7.13	26.53	93.91

Table V-6. Energy Impact from Refrigerated Vent Condenser

Capacity (m^3)	Electrical Requirements (J/g) Case I	Case II	Case III
150	1854	688	511
660	885	456	467
2840	468	331	464

Table V-7. VOC Emissions from Model Floating-Roof Tank vs Absolute Vapor Pressures of Material Stored

	VOC Emissions (Mg/yr) for Vapor Pressures of				
Model Tank Capacity (m^3)	51.7 kPa	69.0 kPa	76.6 kPa	86.2 kPa	100.7 kPa
40	0.58	0.94	1.22	1.86	17.88
75	0.60	0.96	1.23	1.87	17.90
115	0.61	0.98	1.25	1.89	17.92
150	0.75	1.20	1.54	2.33	22.11
285	1.16	1.88	2.43	3.70	35.59
660	1.47	2.40	3.10	4.74	45.66
1420	2.59	4.23	5.48	8.38	80.96
2840	4.31	7.08	9.17	14.05	135.96
8330	9.62	15.83	20.51	31.45	304.88

Emissions were calculated based on the standing-storage- and withdrawal-loss equations discussed in Sect. III of this report for an internal-floating-roof tank.

Two pressure-vessel conditions were evaluated for pressure vessels used in place of internal-floating-roof tanks or open-top floating roof tanks with primary and secondary seals (new sources): no VOC loss (100% emission control) and 98%-controlled VOC emissions. The latter condition would apply to pressure vessels with an inert-gas pad used for safety or operating reasons and that would therefore require periodic relief venting. Table V-8 shows the VOC emission reduction that can be achieved by installation of a new pressure vessel instead of a new floating-roof tank. Both the 98%- and 100%-control conditions are shown.

In operation, pressure vessels used as emission controls do not consume any raw materials or utilities and have no adverse environmental or energy impacts.

2. Loading and Handling

A model loading terminal sized for handling 950 m^3 of organics per day was selected for evaluation of the cost effectiveness of two control methods. The model was selected from the EPA Guideline Series document Control of Hydrocarbons from Tank Truck Gasoline Loading Terminals.[1] The use of this model was considered to be acceptable because petroleum loading operations compare reasonably well with those of the SOCMI.

Two controls taken from the cited document are evaluated: a refrigerated condenser system that condenses VOC vapors at atmospheric pressure and -73°C temperature, and an oxidation system based on a thermal oxidizer.

Table V-9 shows the theoretical control efficiencies of the condenser for the four vapor pressures selected. The control efficiency of the thermal oxidizer was estimated to be 99%.

Table V-10 gives the VOC emissions expected from the model terminal before controls and after either the refrigeration or teh oxidizer system was installed.

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Table V-8. VOC Emission Reduction from Installation of New Pressure Vessels Instead of New Floating-Roof Tanks as a Function of Stored-Material Vapor Pressures

Model Tank Size (m^3)	VOC Emission Reductions (Mg/yr)									
	51.7 kPa		69.0 kPa		76.6 kPa		86.2 kPa		100.7 kPa	
	(98%)	(100%)	(98%)	(100%)	(98%)	(100%)	(98%)	(100%)	(98%)	(100%)
40	0.57	0.58	0.92	0.94	1.19	1.22	1.82	1.86	17.53	17.88
75	0.58	0.60	0.94	0.96	1.21	1.23	1.84	1.88	17.54	17.90
115	0.60	0.61	0.96	0.98	1.23	1.25	1.85	1.89	17.56	17.92
150	0.74	0.75	1.18	1.20	1.51	1.54	2.28	2.33	21.66	22.11
285	1.13	1.16	1.84	1.88	2.38	2.43	3.63	3.70	34.88	35.59
660	1.44	1.47	2.36	2.40	3.04	3.10	4.65	4.74	44.75	45.66
1420	2.53	2.59	4.15	4.24	5.37	5.48	8.21	8.38	79.34	80.96
2840	4.23	4.31	6.94	7.08	8.99	9.17	13.77	14.05	133.24	135.96
8330	9.42	9.62	15.51	15.83	20.10	20.51	30.82	31.45	298.79	304.88

Table V-9. Control Parameters of Model Loading Terminal for Refrigeration System

Theoretical Control Efficiency (%)	Vapor Pressure (kPa)	
	Initial	Final
60	3.5	1.4
86.7	10.3	1.4
93.3	34.5	3.5
94.9	69.0	3.5

Table V-10. VOC Emissions from Model Loading Terminal Before and After Addition of Controls

Vapor Pressure (kPa)	VOC Emission (Mg/yr)		
		After Controls Added	
	Before Controls Added	Refrigeration	Oxidizer System
3.5[a]	15.8	6.3	0.2
10.3[b]	76.3	10.5	0.8
34.5[c]	123.8	8.3	1.2
69.0[d]	267.8	13.7	2.7

[a] Uncontrolled emission rate, 55 mg per liter loaded (derived from Table III-3).

[b] Uncontrolled emission rate, 265 mg per liter loaded (derived from Table III-3).

[c] Uncontrolled emission rate, 430 mg per liter loaded (derived from Table III-3).

[d] Uncontrolled emission rate, 930 mg per liter loaded (derived from Table III-3).

Emissions were calculated with the equations discussed in Sect. III and averaged from the vapor pressures given in Table III-3.

The energy effect of vapor recovery systems at terminals is considered to be minimal. Although energy is required to drive compressors, pumps, and other equipment, in most systems a valuable product is recovered that would otherwise be lost to the atmosphere. In thermal-oxidizer systems additional energy will be required in the form of gaseous fuel to convert the VOC vapor to carbon dioxide and water. An estimated 85 liters of propane per Mg of product per year is required by the oxidizer.[1]

B. CONTROL COST IMPACT

This section presents estimated costs and cost-effectiveness ratios for the additional control of VOC emissions from the storage and loading of organic chemicals in the synthetic organic chemicals industry. Present emission sources and emission quantities are discussed in Sect. III.

The capital cost estimates represent the total investment involved in purchasing and installing all equipment and material necessary for a complete control system that will perform as defined for a new installation at a typical location. These estimates do not include such highly variable costs as loss of production during installation or startup, research and development, land acquisition, and preparation and cleaning of the tanks for retrofitting. Cost estimate calculations are included in Appendix C.

Cost factors for calculation of annual operating costs are shown in Table V-11. The capital recovery factor of 0.18 is based on a 10-year depreciable life and a 12% annual interest rate. Emission recovery credit is based on the average market value of all synthetic organic chemicals that have potential recovery. Annual costs are for a 1-year period beginning in December 1979.

1. Storage Tanks

a. Fixed-Roof-Tank Emission Controls——The capital cost and the cost effectiveness of controlling VOC emission losses with two control techniques were evaluated:

Table V-11. Cost Factors for Computing Annual Costs

Item	Factor
Electrical power	8.33 \$/GJ
Operating time	8760 hr/yr
Operating labor	Minor; not considered
Maitenance material and labor	\$0.06 X capital cost
Capital charges	
Capital recovery	\$0.18 X capital cost
Miscellaneous (taxes, insurance, and administration)	\$0.05 X capital cost
Liquid-waste disposal	Minor; not considered
Recovery credit	\$330.8/Mg

Table V-12. Installed Capital and Operating Costs for Internal-Floating-Roofs[a]

Model Tank Size (m^3)	Installed Capital Cost ($X 10^3$)			Annual Operating Cost[b] ($X 10^3$)
	Floating Roof	Secondary Seal =	Total	
40	5.6	0.6	6.2	1.8
75	5.6	0.6	6.2	1.8
115	5.6	0.6	6.2	1.8
150	6.0	0.6	6.6	1.9
285	7.1	0.9	8.0	2.3
660	8.0	1.0	9.0	2.6
1420	12.0	1.5	13.5	3.9
2840	20.4	2.1	22.5	6.5
8330	50.3	3.6	53.9	15.6

[a] A contact internal floating roof with a secondary seal installed in a fixed-roof tank.

[b] Before credit.

Internal floating roof used on fixed-roof tanks—Table V-12 shows the installed capital cost and the annual operating cost for the installation of a contact internal floating roof with a liquid primary seal and a continuous secondary seal to an existing fixed-roof tank. The annual operating cost is the cost of the internal floating roof before recovery credit is taken for the emission reductions. The installed capital costs for the roof and seal were taken from Table C-1 of Appendix C.

The installed capital costs for tanks shown in Table C-1 were prepared primarily from data presented in the EPA report Volatile Organic Compound Emissions from Organic Liquid Storage Tanks,[2] which was prepared by TRW.

Table V-13 gives the cost effectiveness for installing a floating roof to an existing fixed-roof tank. The cost effectiveness is affected by the vapor pressure of the material stored in the model tank. The cost effectiveness versus tank size is plotted in Fig. V-1.

Refrigerated vent condensers (new and retrofit sources)——To evaluate the control cost effectiveness of adding a refrigerated vent condenser to a new or existing fixed-roof tank, the models and conditions discussed in the environmental and energy impact portion of this section were used; see Tables V-4—V-6.

Table V-14 gives the cost effectiveness for adding refrigerated vent condensers to the fixed-roof model tanks for all three cases. Cost estimation details are given in Appendix C. Figure V-2 is a plot of the cost effectiveness for the three model conditions.

The cost effectiveness for multiple storage tanks containing the same material and using a common add-on refrigeration unit should be more favorable than that for equivalent storage tanks using individual controls. These highly variable situations were not modeled.

Other control techniques——Due to time limitations cost-effectiveness calculations were not completed for carbon adsorption and thermal oxidation. Installed capital cost curves for both techniques are, however, included in the cost estimate details (Appendix C).

Table V-13. Cost Effectiveness of Installing an Internal Floating Roof in a Fixed Roof-Tank

Model Tank Size (m3)	Cost Effectiveness ($/Mg) at Vapor Pressures of						
	1.0 kPa	1.4 kPa	3.4 kPa	6.9 kPa	10.3 kPa	34.5 kPa	51.7 kPa
40	12,530	9665	4815	2625	1650	580	270
75	6,590	5125	2395	1195	700	140	(20)[a]
115	4,535	3420	1485	710	370	(15)	(120)
150	3,545	2590	1190	485	220	(80)	(165)
285	2,820	2090	880	360	135	(115)	(190)
660	1,555	1115	390	80	(55)	(205)	(245)
1420	1,085	750	40	(25)	(125)	(235)	(265)
2840	1,325	940	310	40	(80)	(215)	(255)
8330	1,985	1460	605	215	40	(155)	(215)

[a] Values in parentheses represent credits.

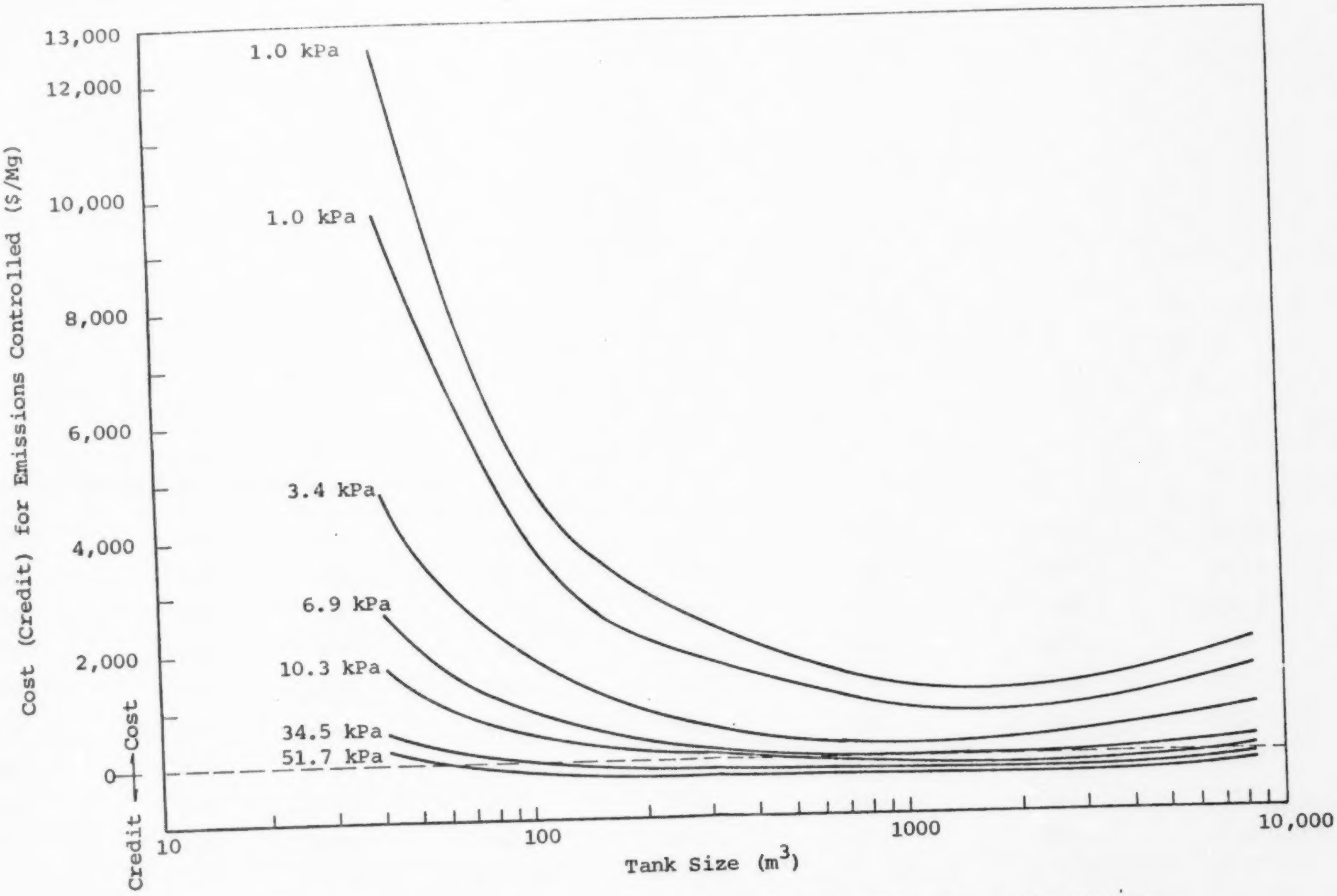

Fig. V-1. Cost Effectiveness of Controlling Emissions by Retrofitting Existing Fixed-Roof Tank with Internal Floating Roofs

Table V-14. Cost Effectiveness for Add-On Refrigerated Vent Condenser to Fixed-Roof Tank (New and Retrofitted Sources)

Model Tank Size (m^3)	Cost Effectiveness* (per Mg)		
	Case 1	Case 2	Case 3
150	$10,430	$3,031	$1,693
660	8,030	2,470	2,585
2840	5,245	1,890	2,085

*Case conditions described in Table V-4.

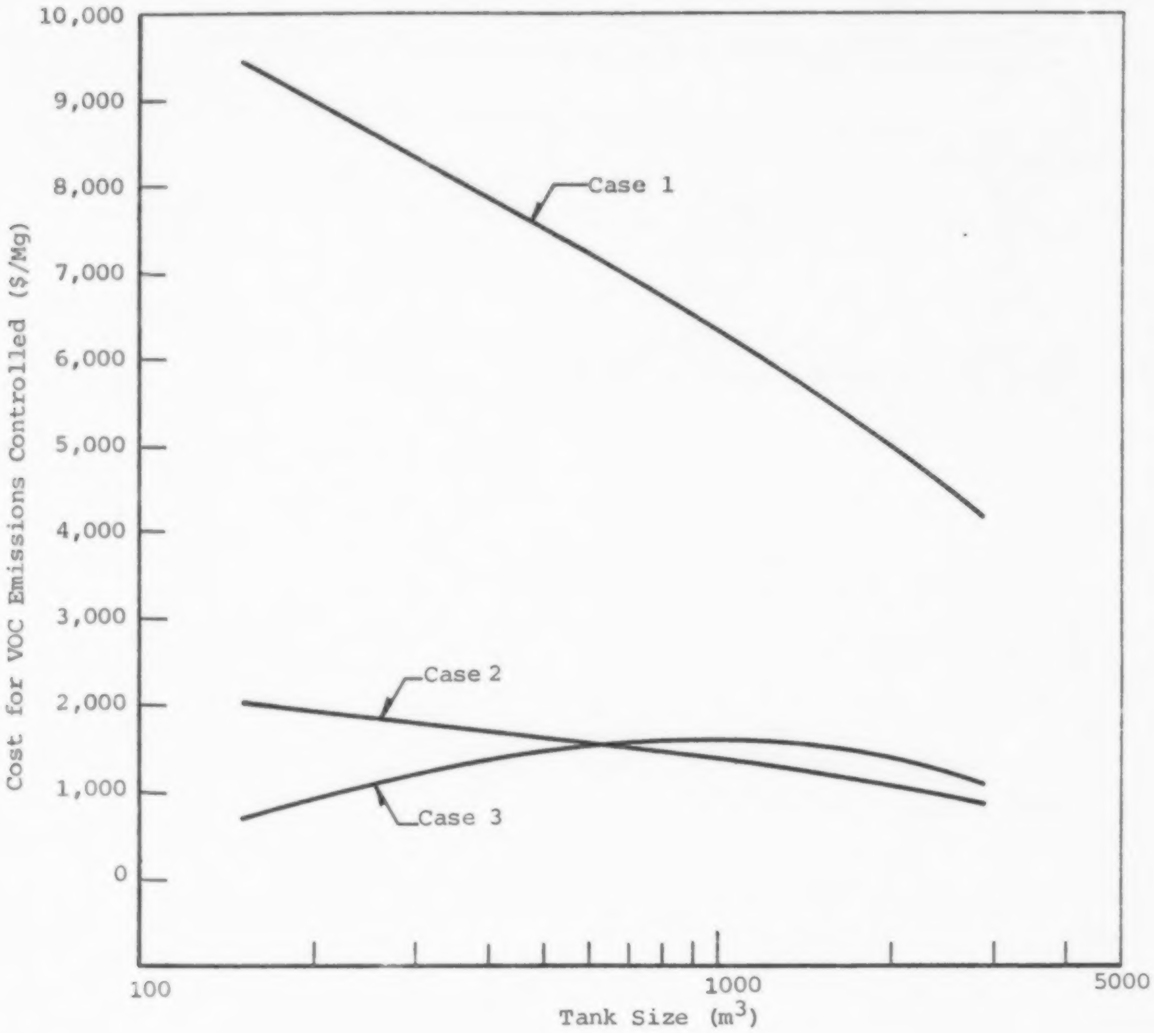

Fig. V-2. Cost Effectiveness of Controlling Emissions by Refrigerated Vent Condenser Added On to Fixed-Roof Tank

b. Floating-Roof-Tank Emission Controls——The capital cost and the cost effectiveness of controlling VOC emission losses from an internal floating-roof tank were evaluated:

To evaluate the control cost effectiveness of installing new, low-pressure service (172 kPa maximum) vessels instead of new floating-roof tanks, the models and emission reductions discussed in Sect V-A were used. The annual operating cost was calculated from the incremental capital cost difference between a new, internal-floating-roof tank and a new pressure vessel.

Table V-15 shows the installed capital cost and the annual operating cost, before credit was taken for emission recovery, for each of the model tank sizes.

Installed capital costs are based on the cost data for fixed-roof tanks factored by engineering estimates to represent current low-pressure service vessel costs. Cost estimation details are given in Appendix C.

Table V-16 gives the cost effectiveness for installing new pressure vessels at the 98%- and 100%-control conditions. Figures V-3 and V-4 are plots of the cost effectiveness for the new-pressure-vessel installation at 98%- and 100%-control efficiency conditions respectively.

2. Loading and Handling

To evaluate the control cost effectiveness of installing either the refrigeration or oxidizer system for loading terminals, the model and emission reductions described in Sect. V-A were used.

All installed capital cost and operating cost data shown in Table V-17 were taken from the EPA Guideline series document Control of Hydrocarbons from Tank Truck Gasoline Unloading Terminals[1] and adjusted to reflect December 1979 dollars.

Table V-18 gives the cost effectiveness for installing either the refrigeration or the oxidizer system at the model terminal for loading chemicals with four selected vapor pressures.

Table V-15. Installed Capital and Operating Costs for Pressure Vessels

Model Tank Capacity (m^3)	Installed Capital Cost (X 10^3)[a]	Annual Operating Cost (X 10^3)[b]
40	$ 7.8	$ 2.3
75	5.8	1.7
115	4.2	1.2
150	6.8	2.0
285	14.0	4.1
660	34.5	10.0
1420	64.6	18.7
2840	102.9	29.8
8330	242.7	70.4

[a] Incremental cost difference between new pressure vessel and new floating-roof tank.

[b] 29.0% of capital cost before recovery credit.

Table V-16. Cost Effectiveness for Installing a New Pressure Vessel Instead of a New Floating-Roof Tank (Incremental Cost Difference) as a Function of Stored-Material Vapor Pressures

Model Tank Size (m^3)	Cost Effectiveness (per Mg)									
	98% Control Efficiency at Vapor Pressures of					100% Control Efficiency at Vapor Pressures of				
	51.7 kPa	69.0 kPa	76.6 kPa	86.2 kPa	100.7 kPa	51.7 kPa	69.0 kPa	76.6 kPa	86.2 kPa	100.7 kPa
40	$3704	$2167	$1593	$ 933	($200)*	$3627	$2123	$1561	$ 914	($202)
75	2573	1489	1075	600	(234)	2521	1460	1053	587	(235)
115	1667	941	652	324	(262)	1634	922	639	317	(265)
150	2446	1361	995	526	(240)	2397	1333	975	515	(240)
285	3263	1898	1387	800	(212)	3198	1860	1359	756	(214)
660	6579	3907	2959	1830	(107)	6450	3829	2900	1772	(112)
1420	7067	4169	3148	1948	(95)	6886	4085	3085	1897	(100)
2840	6722	3963	2982	1838	(107)	6588	3883	3422	1794	(112)
8330	7142	4209	3169	1953	(95)	6989	4119	3100	1908	(100)

*Values in parentheses represent credits.

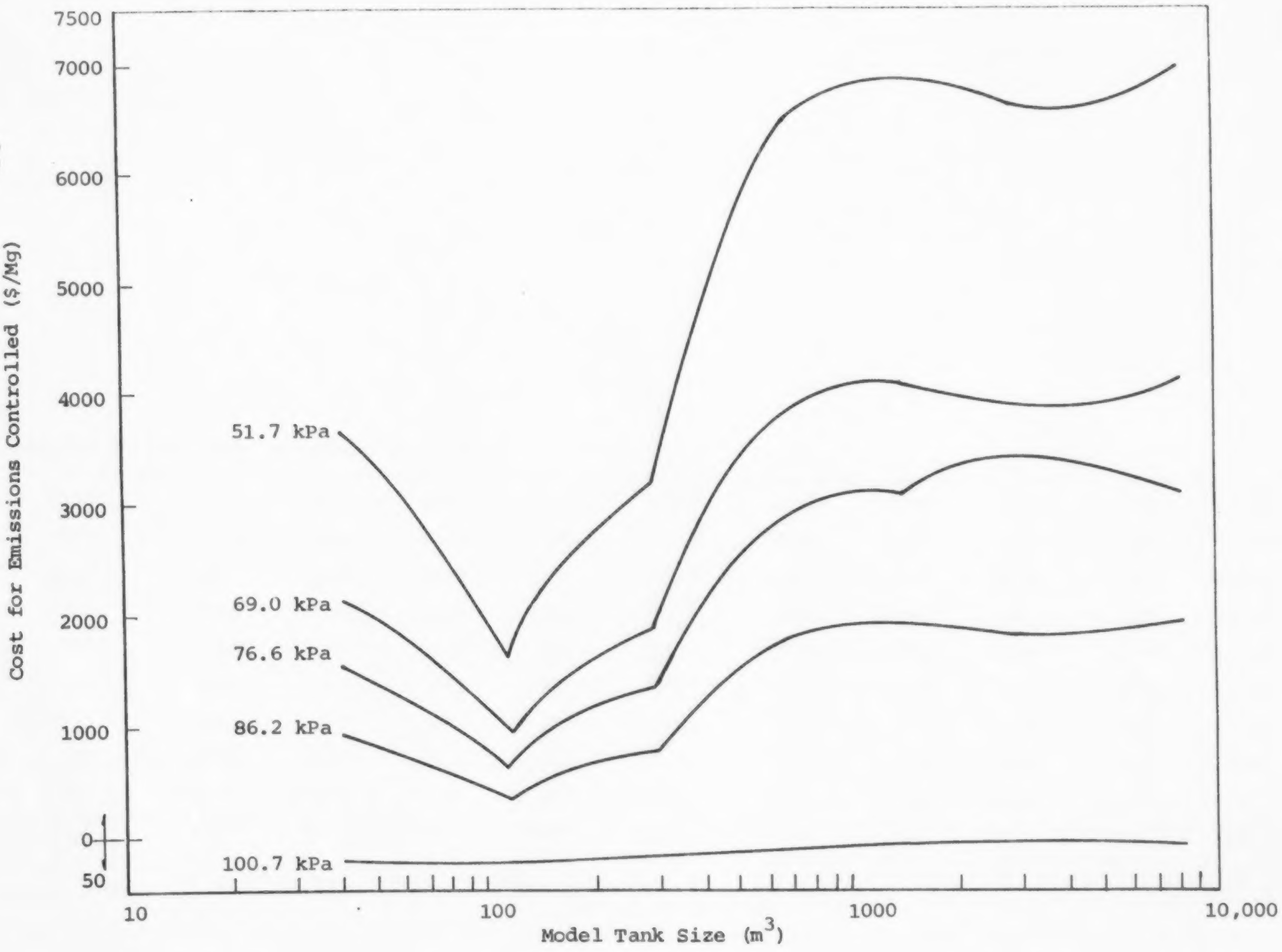

Fig. V-3. Cost Effectiveness of Controlling Emissions (100%) by Installing New Pressure Vessel vs New Floating-Roof Tank

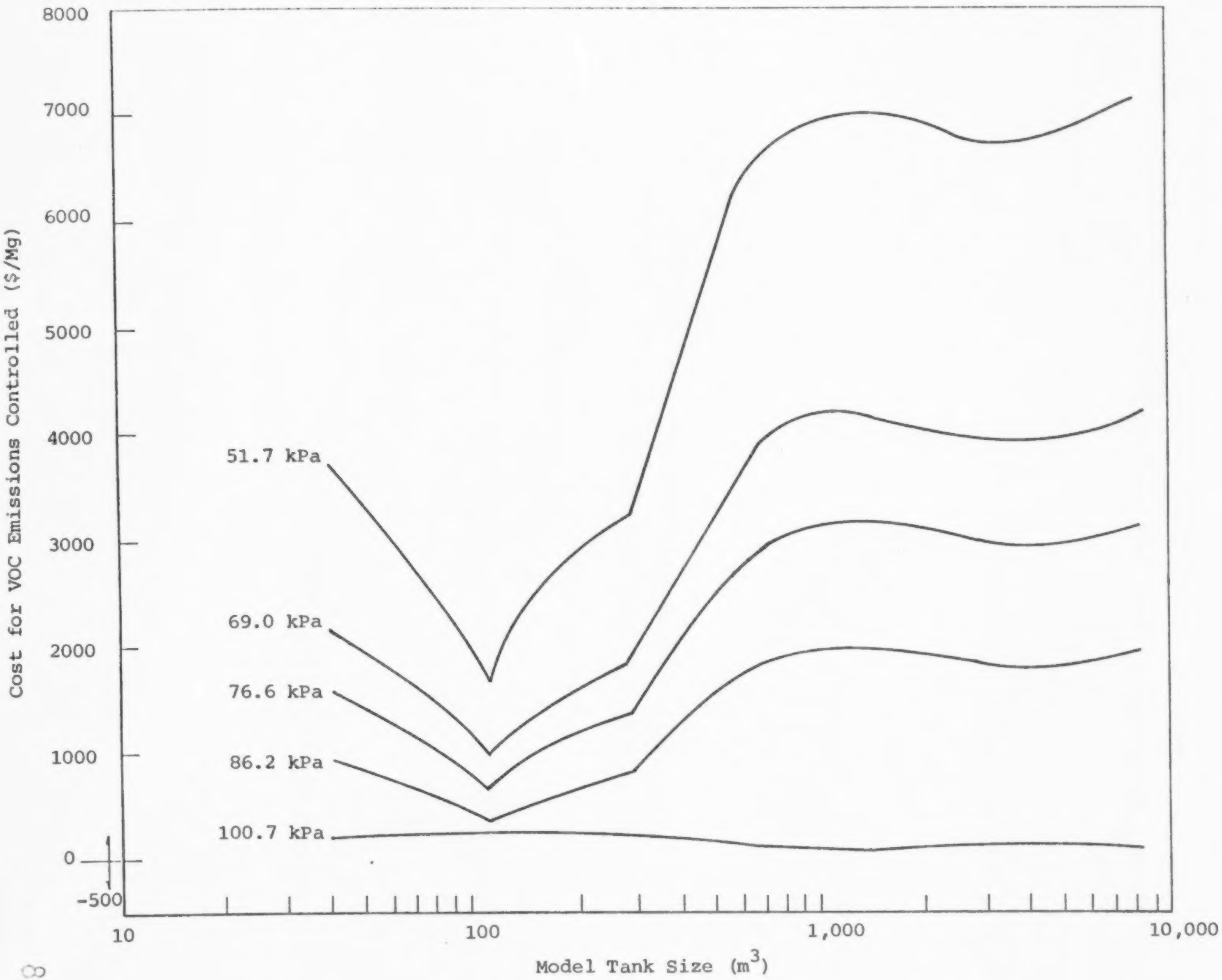

Fig. V-4. Cost Effectiveness of Controlling Emissions (98%) by Installing New Pressure Vessel vs New Floating-Roof Tank

Table V-17. Installed Capital and Operating Cost for Model-Loading-Terminal[a] Control Systems (950 m^3/day)

Control System	Installed Capital Cost (X 10^3)	Annual Operating Cost (X 10^3)[b]
Refrigeration	$186.6	$54.1
Oxidizer	148.4	43.0

[a] Top-submerged or bottom-filled.
[b] Based on 29.0% of capital before recovery credit.

Table V-18. Cost Effectiveness for Loading-Terminal (950 m^3/day) Control Systems vs Material Vapor Pressures

Vapor Pressure (kPa)	Cost Effectiveness (per Mg)	
	Refrigeration System	Oxidizer System
3.5	$5368	$2756
10.3	491	570
34.5	138	351
69.0	(118)*	162

*Values in parentheses represent credits.

C. REFERENCES*

1. Control of Hydrocarbons from Tank Truck Gasoline Loading Terminals, Guideline Series, EPA-450/2-77-026 (OAQPS No. 1.2-082), Research Triangle Park, NC (October 1977).

2. Volatile Organic Compound Emissions from Volatile Organic Liquid Storage Tanks, draft, chapters 3—6 and preliminary capital costing, Apr. 28, 1980 (on file at EPA, ESED, Research Triangle Park, NC).

*A reference located at the end of a paragraph usually refers to the entire paragraph. If another reference relates to certain portions of the paragraph, the reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VI. ASSESSMENT

A. SUMMARY

1. Storage

The synthetic organic chemicals industry currently uses a total of 20,270 fixed-roof tanks, floating-roof tanks, and pressure vessels for VOC storage. The primary type of storage vessel utilized by the industry is the fixed-roof tank. It comprises 73% of the total number of storage vessels and contributes 61% of the total storage volume. Its primary drawback is its high susceptibility to breathing and working losses. The emission sources and control levels for industry storage are shown in Tables III-4 and III-5. Current emissions for all industrial storage are estimated to be 31,413 Mg/yr. Fixed-roof tanks account for an estimated 94% of the total storage VOC losses.

Pressure vessels are the most efficient storage tanks and have negligible emissions during normal operation. The use of internal-floating-roof tanks is a significant control measure, with internal floating roofs being an average of 85% more effective in controlling VOC emissions than fixed-roof tanks. Refrigerated vent condensers are one of the most common types of control devices now in use on fixed-roof tanks with control.

Fixed-roof-tank emissions can be controlled by means of internal-floating-roof tanks and refrigerated vent condensers in a new plant or by retrofitting floating roofs or refrigerated vent condensers on existing fixed-roof tanks. The emission reduction would be 76% to 97% for floating roofs and 60% to 95%+ for refrigerated vent condensers. The cost effectiveness for installing internal floating roofs can yield credits ($200+/Mg) at high vapor pressures. Refrigerated vent condensers on individual fixed-roof tanks are not as cost effective as floating-roof tanks.

Floating-roof-tank emissions can be eliminated by installation of pressure vessels in new plants. Cost effectiveness for pressure vessels is most favorable at high vapor pressures and small tank sizes.

2. Loading

An estimated 3,393,100 Mg of synthetic organic material is shipped by the industry. Cargo carriers include tank cars, tank trucks, and marine vessels, with water transportation accounting for 50% of the total volume of chemicals shipped. An estimated 81% of all chemicals shipped have vapor pressures of less than 34.5 kPa.

The emission sources and control levels for the industry loading are shown in Fig. III-6. Current emissions for all chemical loading and transport are estimated to be 4917 Mg/yr.

The industry currently uses both splash-filling and submerged- or bottom-filling methods for loading all types of carriers with a wide vapor pressure range of chemicals. The use of refrigerated condensers or of a vapor oxidizer is a significant control measure when applied to chemicals with vapor pressures in excess of 3.5 kPa. VOC emission reductions of 70 to 90% are possible. The use of pressurized carriers eliminates transit losses.

Refrigerated condensers systems can have favorable cost effectiveness if used on high-vapor-pressure materials, yielding credits as high as $120 per Mg of VOC controlled.

B. SUPPLEMENTAL INFORMATION

The primary basis for characterization of the storage and handling segment of the SOCMI was the State Emissions Inventory files obtained from Texas and Louisiana. It would be appropriate to update the present data base when supplemental tank data from additional site visits resulting from new-product study assignments and other State Emissions Inventory files become available.

APPENDIX A

EMISSION CALCULATION SUPPLEMENTS

Table A-1. Paint Factors for Fixed-Roof Tanks

Tank Color		Paint Factors (F_p)	
		Paint Condition	
Roof	Shell	Good	Poor
White	White	1.00	1.15
Aluminum (specular)	White	1.04	1.18
White	Aluminum (specular)	1.16	1.24
Aluminum (specular)	Aluminum (specular)	1.20	1.29
White	Aluminum (diffuse)	1.30	1.38
Aluminum (diffuse)	Aluminum (diffuse)	1.39	1.46
White	Gray	1.30	1.38
Light gray	Light gray	1.33	1.44*
Medium gray	Medium gray	1.40	1.58*

*Estimated from the ratios of the seven preceding paint factors.

Table A-2. Tank, Type, Seal, and Paint Factors for Floating-Roof Tanks

Tank Type	K_t*	Seal Type	K_s*	Painted Color of Shell and Roof	K_y*
Welded tank with pan or pontoon roof, single or double seal	0.0045	Tight fitting (typical of modern metallic and non-metallic seals)	1.00		
Riveted tank with pontoon roof, double seal	0.11	Loose fitting (typical of seals built prior to 1942)	1.33		
Riveted tank with pontoon roof, single seal	0.13				
Riveted tank with pan roof, double seal	0.13			Light gray or aluminum	1.0
Riveted tank with pan roof, single seal	0.14			White	0.9

*See "Calculations" in Sect. III.

Table A-3. S Factors for Calculating Petroleum Loading Losses

Cargo Carrier	Mode of Operation	S Factor
Tank trucks and tank cars	Submerged loading of a clean cargo tank	0.50
	Splash loading of a clean cargo tank	1.45
	Submerged loading: normal dedicated service	0.60
	Splash loading: normal dedicated service	1.45
	Submerged loading: dedicated, vapor balance service	1.00
	Splash loading: dedicated vapor balance service	1.00
Marine vessels	Submerged loading: ships	0.2
	Submerged loading: barges	0.5

*Saturation factor; see "Calculations" in Sect. III.

APPENDIX B

ALTERNATIVE FLOATING-ROOF-TANK EMISSION ESTIMATION EQUATIONS

FLOATING-ROOF-TANK EMISSIONS EQUATIONS

VOC emissions from external-floating-roof, noncontact internal-floating-roof, and contact internal-floating-roof storage tanks can be estimated with equations based on a pilot test tank study conducted for EPA.[1]

From the equations presented below, it is possible to estimate the total evaporation loss (L_T), which is the sum of the withdrawal loss (L_{WD}), the seal loss (L_S), and the fitting loss (L_F):

$$L_T = L_{WD} + L_S + L_F,$$

$$L_S = K_S V^n M_V D \quad \frac{\frac{P}{(14.7)}}{[1 + (1 - \frac{P}{14.7})^{0.5}]^2} \quad \frac{1}{2205},$$

$$L_F = NK_F V^n M_V \quad \frac{\frac{P}{(14.7)}}{[1 + (1 - \frac{P}{14.7} \; 0.5]^2} \quad \frac{1}{2205},$$

where

L_T = total loss (Mg/yr);

L_{WD} = withdrawal loss (Mg/yr);

L_S = seal loss (Mg/yr);

L_F = fitting loss (Mg/yr);

M_V = molecular weight of product vapor (lb/lb-mole); 78.1 lb/lb-mole for VOC;

P = true vapor pressure of product (psia); 2 psia assumed;

D = tank diameter (ft);

W_L = density of product (lb/gal); 7.37 lb/gal for VOC;

V = average wind speed for the tank site (mph); 10 mph assumed average wind speed;

Q = product average throughput (bbl/yr); tank capacity (bbl/turnover) X turnovers/yr;

---

[1] Chicago Bridge and Iron Co., Plainfield, IL, Hydrocarbon Emission Loss on a 20 Foot Diameter Pilot Test Tank with an Ultraflash and a CBI Weathermaster Internal Floating Roof, R-0113/R-0191 (June 1978).

K_S = seal factor; see Table B-1;

K_F = fitting factor; see Table B-2;

n = seal wind speed exponent; see Table B-1;

m = fitting wind speed exponent; see Table B-2;

C = product withdrawal shell clingage factor [bbl/(ft^2 X 10^3)]; use 0.0015 bbl/(ft^2 X 10^3) for VOC in a welded steel tank with light rust;

N = fitting multiplier; see Table B-3.

Table B-1. Emission Factors K_S and n[1]

Roof and Seal Combinations	K_S[a]	n[b]
Contact internal floating roof		
Liquid-mounted primary seal only	12.7	0.4
Liquid-mounted primary seal and continuous secondary seal	3.6	0.7
Non-contact internal floating roof with vapor-mounted primary and secondary seals	10.3	1.0
External floating roof		
Primary seal only	48.6	0.7
Primary and secondary seals	57.7	0.2

[a] K_S = seal factor.

[b] n = seal wind speed exponent.

Table B-2. Summary of Emission Factors K_F and m For Floating Roofs[1]

Case Number	Roof Description	K_F[a]	m[b]
1	Contact internal floating roof	132	0
2	Non-contact internal floating roof	309	0.3
3	External floating roof	0	0

[a] K_F = fitting factor.

[b] m = fitting wind speed exponent.

Table B-3. Fitting Multipliers[1]

D Tank Diameter (ft)	N Fitting Multiplier
< D < 20	0.5
20 < D < 75	1
75 < D < 100	2
100 < D < 120	3
125 < D < 150	4
150 < D < 175	5
175 < D < 200	6

---

[1] Chicago Bridge and Iron Company. Hydrocarbon Emission Loss Measurements on a 20 Foot Diameter Pilot Test Tank with an Ultraflote and a CBI Weathermaster Internal Floating Roof. Report No. R-0113/R-0191. Plainfield, Illinois. Juen 1978.

APPENDIX C

COST ESTIMATE DETAILS AND CALCULATIONS
FLOATING ROOF - REFRIGERATED VENT CONDENSER - PRESSURE VESSEL

COST ESTIMATE DETAILS

This appendix contains the details of the estimated costs presented in this report.

Installed capital costs for fixed-roof tanks, floating roofs and secondary seals were derived from Tables C-1 through C-4. These tables were obtained from an EPA, ESED draft report, Volatile Organic Compound Emissions from Volatile Organic Liquid Storage Tanks.

The refrigerated vent condenser installed capital costs shown on the evaluation sheets were derived from the cost curves shown in Figs. C-1 and C-2 and includes the capital required for installing a condenser and a refrigeration system. The curves were taken from the Condensation, Control Device Evaluation report prepared by IT Enviroscience for EPA, ESED in Research Triangle Park, NC.

Pressure vessel installed capital costs were obtained by applying engineering estimates to floating-roof tank costs. The methodology is shown in Table C-5.

Also included in this Appendix are installed capital cost curves for a carbon adsorption unit (Fig. C-3) and thermal oxidation unit (Fig. C-4). They were obtained from the Carbon Adsorption Control Device Evaluation report, and from The Thermal Oxidation Control Device Evaluation report, both prepared by IT Enviroscience for the EPA, ESED in Research Triangle Park, NC.

Table C1. COST[a] OF BUILDING A FIXED ROOF TANK[b]

Diameter (ft)	Height (ft)	Installed cost[c]
20	24	26,000
40	40	63,000
45	40	73,000
50	40	89,000
60	40	113,000
70	40	139,000
80	40	168,000
90	40	202,000

[a] Costs obtained from Thomas Tremblay, of Chicago Bridge and Iron, February 27, 1980.

[b] Equation derived from the available data.
$\text{Cost}\ (\$) = -1783.02 + (1.099 \times 10^3 \times D) + (14.028 \times D^2) - (.01301 \times D^3)$
where D = diameter in feet.

[c] Costs in first quarter 1980 dollars.

Table C2. COST[a] OF INSTALLING A CONTACT SINGLE SEAL INTERNAL FLOATING ROOF[b]

Diamter (ft)[c]	Installed cost ($)[d]
15	5,630
20	6,485
25	7,510
30	8,780
35	10,280
40	11,970
45	14,180
50	16,190
55	19,630
60	21,480
65	25,120
70	27,770
75	31,240
80	34,360
85	37,910
90	41,530

---

[a] Cost obtained from Bill Blumquist, of Petrex, February 20, 1980.

[b] Equation derived from available data.
$\text{Cost } (\$) = 5761 - (58.15 \times D) + (5.335 \times D^2)$.

[c] Cost of adding a secondary seal, per foot of circumference is $11.85.

[d] Costs in first quarter 1980 dollars.

Table C3. COST[a] OF INSTALLING A NON-CONTACT SINGLE SEAL INTERNAL FLOATING ROOF[b]

Diameter (ft)[c]	Installed cost ($)[d]
15	4,500
20	6,000
25	7,300
30	9,300
35	10,000
40	12,000
45	13,300
50	14,700
55	16,500
60	17,400
65	19,700
70	21,500
75	23,500
80	25,200
85	27,800
90	30,000

[a] Cost obtained from Henry Reiss, of Altech Industries, Inc., February 26, 1980.

[b] Equation derived from available data.
Cost ($) = 1614.3 + (198.5 x D) + (1.26 x D^2).

[c] Installed cost of adding a secondary wiper seal per foot of circumference is $22.50.

[d] Costs in first quarter 1980 dollars.

Table C4. COST[a] OF BUILDING AN EXTERNAL FLOATING ROOF TANK[b]

Diameter (ft)[c]	Height (ft)	Installed Cost[d]
30	24	40,000
35	30	54,000
42.6	40	81,000
52	40	117,000
60	40	126,000
67	40	140,000
73.4	40	153,000
100	40	212,000

[a] Costs obtained from George Stilt, of Pittsburg Des Moines, April 10, 1980.

[b] Equation derived from available data.
$D \leq 60$ $\text{COST} = -22.2587 \times D^2 + 4869.95 \times D - 86065.68$
$D > 60$ $\text{COST} = 5.078 \times D^2 + 1337.52 \times D + 27467.96$
where D = diameter in feet

[c] Cost of adding a secondary seal per foot of circumference is $13.50.

[d] Costs in first quarter 1980 dollars.

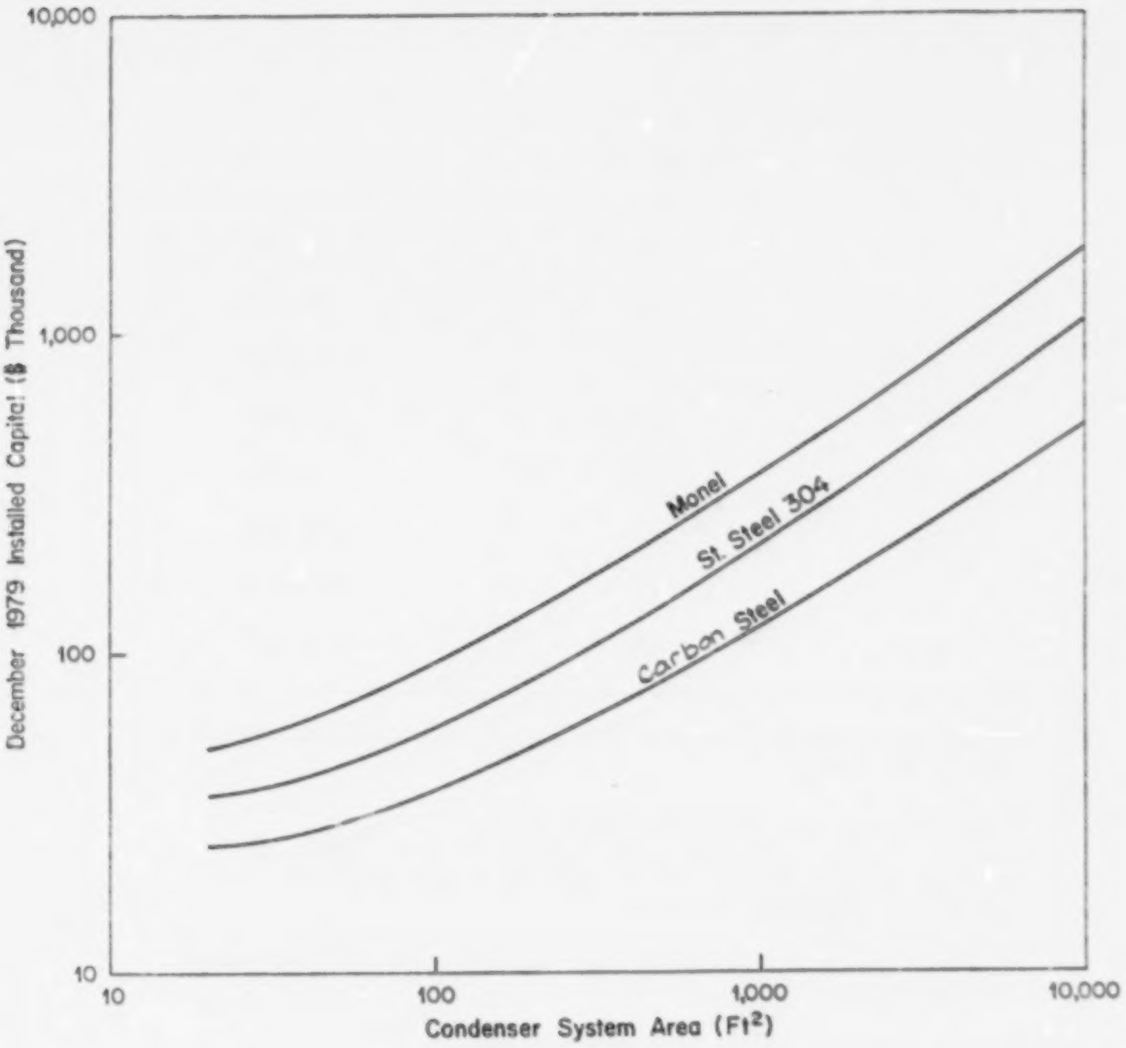

Fig. C-1. Installed Capital Cost vs Condenser Area for Various Materials of Construction for a Complete Condenser Section

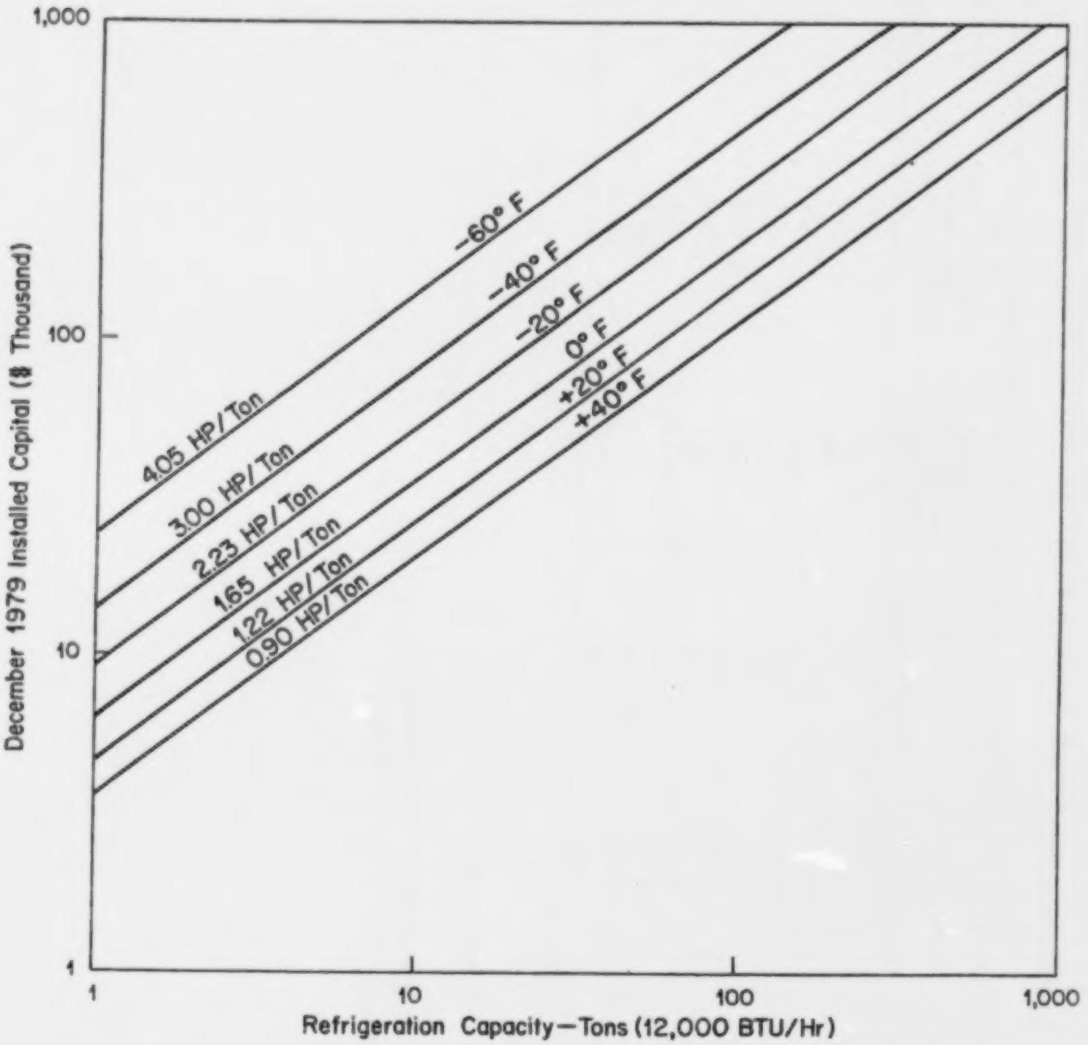

Fig. C-2. Installed Capital Costs vs Refrigeration Capacity at Various Coolant Temperatures for a Complete Refrigeration Section

Table C-5. Pressure Vessel vs Floating-Roof Tank Installed Capital and Operating Cost Differential

Tank Size 10^3 gal	Fixed Roof[a] Installed Capital (10^3 $)	Floating-Roof Plus[b] Secondary Seal Installed Capital (10^3 $)	Floating-Roof[c] Tank Installed Capital (10^3 $)	25 psi[d] Pressure Vessel Scaleup Factor	25 psi[e] Pressure Vessel Installed Capital (10^3 $)	25 psi Pressure Vessel Incremental Capital Difference[f] (10^3 $)	(29.0% of Capital) Annual Operating Cost (10^3 $/yr)
10	17.8	6.2	24.0	1.32	31.8	7.8	2.3
20	17.8	6.2	24.0	1.24	29.8	5.8	1.7
30	17.8	6.2	24.0	1.18	28.2	4.2	1.2
40	20.9	6.6	27.5	1.25	34.3	6.8	2.0
75	30.8	8.0	38.8	1.36	52.8	14.0	4.1
175	37.9	9.0	46.9	1.74	81.4	34.5	10.0
375	63.8	13.5	77.3	1.84	141.9	64.6	18.7
750	104.0	22.5	126.5	1.81	229.4	102.9	29.8
2200	224.9	53.9	278.8	1.87	521/5	242.7	70.4

[a] From Table C-1.

[b] From Table C-2.

[c] Total of fixed-roof tank plus floating-roof and secondary seal.

[d] Based on IT Enviroscience engineering estimates.

[e] Obtained by multiplying scaleup factor times floating-roof tank installed capital.

[f] Difference between pressure vessel and floating-roof tank installed capital.

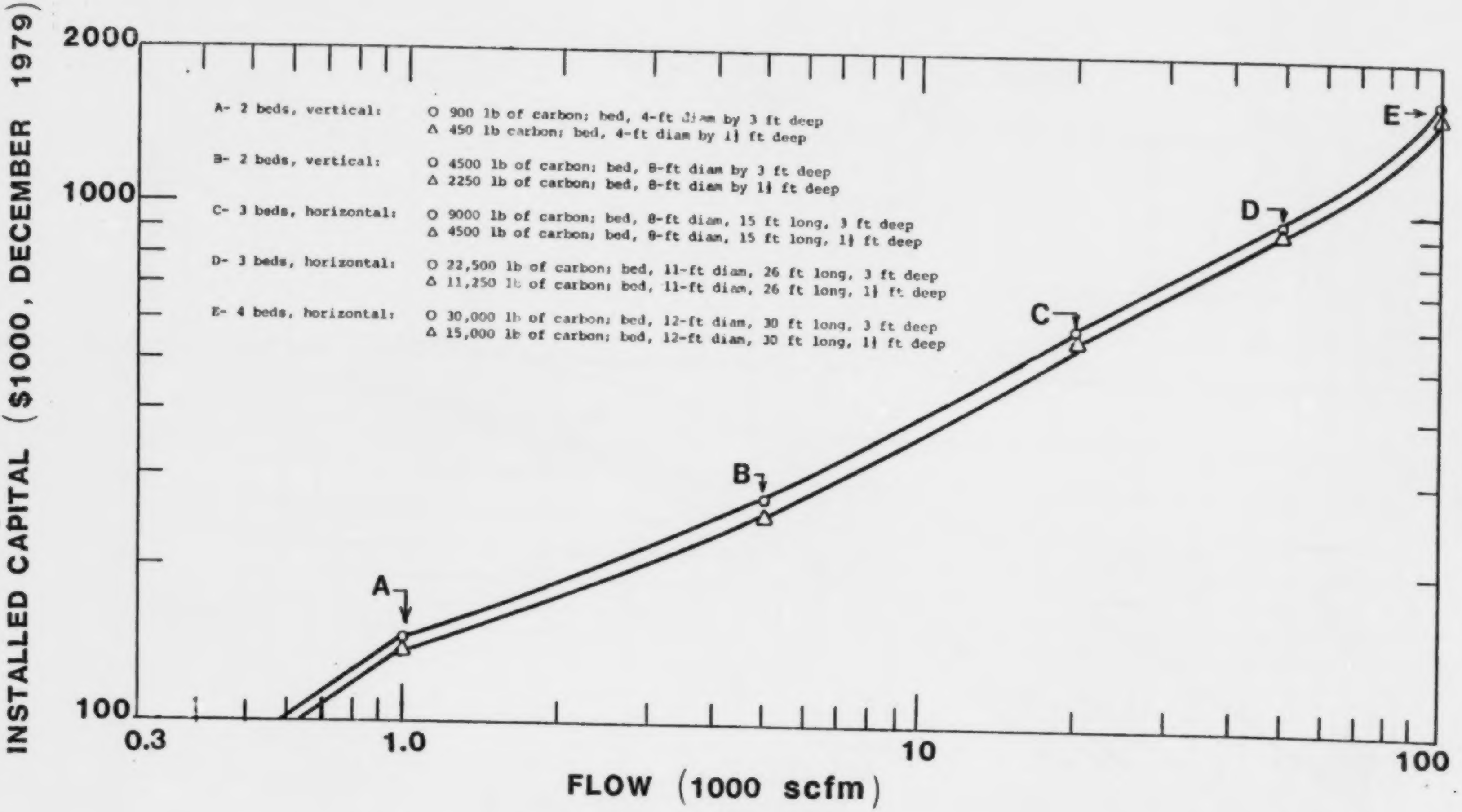

Fig. C-3. Installed Capital Cost of Carbon Adsorption Systems

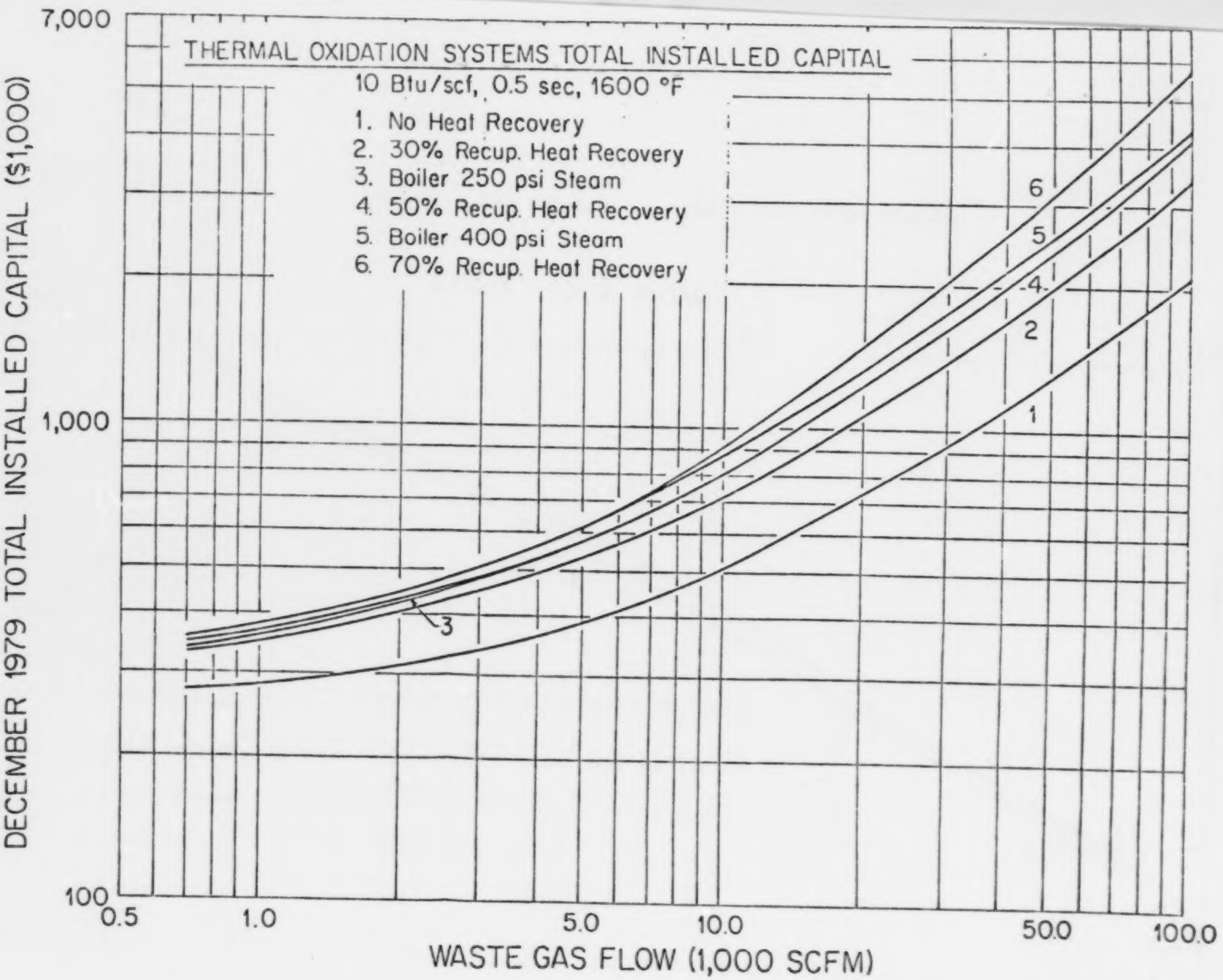

Fig. C-4. Total Installed Capital Cost for Thermal Oxidation Systems with Waste-Gas Heat Content = 10 Btu/scf, Residence Time = 0.5 sec, and Combustion Temperature = 1600°F

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TANK SIZE 10^3 GAL	CASE - 1 - 30% E, 0.5 IVP, 0.2 FVP (PSIA) 26.7 I.Temp, 10 F.Temp (°C) 3.4 % Saturation	CASE - 2 - 86.7% E, 1.5 IVP, 0.2 FVP (PSIA) 26.7 I Temp., -9.6 F Temp. (°C) 10% Saturation	CASE - 3 - 93.3% E, 7.5 IVP, 0.5 FVP (PSIA) 26.7 I Temp., -28.3 F Temp (°C) 51% Saturation
40	0.11 Ton Refrigerator 60 Ft^2 Condenser 1 GPM, $\frac{1}{8}$ HP, Pump Cap = 73M$	0.38 Ton Refrigerator 99 Ft^2 Condenser 1 GPM $\frac{1}{8}$ HP Pump Cap: 85M$	1.6 Ton Refrigerator 107 Ft^2 Condenser 1 GPM, $\frac{1}{8}$ HP Pump Cap = 104M$
175	0.70 Ton Refrigerator 380 Ft^2 Condenser 1 GPM, $\frac{1}{8}$ HP Pump Cap = 108M$	1.9 Ton Refrigerator 503 Ft^2 Condenser 1 GPM, $\frac{1}{8}$ HP Pump Cap = 136M$	8.5 Ton Refrigerator 1063 Ft^2 Condenser 1 GPM, $\frac{1}{8}$ HP Pump Cap: 254M$
750	2.1 Ton Refrigerator 1180 Ft^2 Condenser 1 GPM, $\frac{1}{8}$ HP Pump Cap: 170M$	7.1 Ton Refrigerator 1867 Ft^2 Condenser 1 GPM, $\frac{1}{8}$ HP Pump. Cap = 270M$	31.7 Ton Refrigerator 3956 Ft^2 Condenser 2 GPM, $\frac{1}{4}$ HP Pump Cap: 572M$
40	2.225 TPY HC Emissions 556 Hr/Yr Operating 1.335 TPY HC Recovered 4.8 Lb/Hr " "	5.524 TPY HC Emissions 507 Hr/Yr Operating 4.789 TPY HC Recovered 18.9 Lb/Hr " "	17.961 TPY HC Emissions 507 Hr/Yr Operating 16.758 TPY HC Recovered 66.1 Lb/Hr " "
175	6.603 TPY HC Emissions 295 Hr/Yr Operating 3.962 TPY HC Recovered 26.9 Lb/Hr " "	16.023 TPY HC Emissions 288 Hr/Yr Operating 13.892 TPY Recovered 96.5 Lb/Hr "	51.726 TPY HC Emissions 280 Hr/Yr Operating 48.480 TPY HC Recovered 346.3 Lb/Hr " "
750	19.968 TPY HC Emissions 259 Hr/Yr Operating 11.981 TPY HC Recovered 92.5 Lb/Hr " "	47.471 TPY HC Emissions 230 Hr/Yr Operating 41.157 TPY HC Recovered 257.9 Lb/Hr " "	152.253 TPY HC Emissions 221 Hr/Yr Operating 142.052 TPY HC Recovered 1285.5 Lb/Hr " "

NOTES :-

1. %E x TPY Emissions = HC Recovered
2. Pump HP based [illegible] specific gravity = 1, [illegible], with intermitt. operation
3. Installed capital [illegible] Each installation contains listed equipment items with piping, insulation & instruments + allowance for hazardous area, magnetic [illegible]

Hydroscience Environmental Systems

STORAGE ~ HANDLING
REFRIGERATED CONDENSING SYSTEMS

J.R.F.
5101
5-11-78

Storage Tank Refrigerator Systems
Utility ~ Power Use

9101 J.R.F. 5-11-78

All Per Year.

CASE I

40M Gal.

Pump Power = $5.2 \times 10^{-5} \times 4.8$ #/h × 556 h/yr - - - - - - - - - none

Ref. Power = 0.67 x 0.11 Ton x " " - - - - - - - - 41 KWH

Yard Light & Instruments 0.1 KW × 8760 × 50% ON - - 438 "

1 - (40) ⟶ 479 "

175M Gal.

Pump Power - none

Ref. Power = 0.9 x .7 Ton x 295 hr/y - - - - - - 186 KWH

Yard Lt Inst. 438 "

1 - (175) ⟶ 624 "

750M Gal.

Pump Pwr = $5.2 \times 10^{-5} \times 92.5$ #/h x 259 h/y - - - - - none

Ref. " = 0.9 x 2.1 T x 259 h/y - - - - - 490 KWH

Yard L. + Inst. 438 "

1 - (750) ⟶ 928 "

CASE 2

40M Gal. = 5.2×10^{-5} x 18.9 x 507 - - - - - - - - none

Ref. Pwr = 1.231 x .38 x 507 - - - - - - - 237 KWH

Yard L & Inst - - - 438 "

3 - (40) ⟶ 675 "

175M Gal.

Ref. = 1.231 x 1.9 T x 288 hr - - - 673 KWH

+ 438 "

3 - (175) ⟶ 1211 "

750 M Gal

Ref = 1.231 x 7.1 Ton x 230 hr. - - - - - 2010 KWH

438

3 - (750) ⟶ 2439

Case 3

40M Gal.

1.664 x 1.6 x 506 = 1347 KWH, 1.664 x 8.5 x 280 = 3960, 1.664 x 31.7 x 221

+ 438 " + 438

6 - (40) ⟶ 1785 " 6 - (175) ⟶ 4398 KWH

= 11,657

433

6 - (750) ⟶ 12,090 KWH

STORAGE & HANDLING, REFRIGERATED CONDENSING SYSTEMS

EVALUATION SHEET. CASE NO. 1

	For 40M Gal Tk	For 175M Gal Tk	For 750 Gal Tk.
WASTE & RATE OF HDLG.			
DEC. 1979 INSTALLED CAPITAL COST	34,000	73,000	137,200
UTILITIES:			
Power @ $0.05/kWH	Neg.	Neg.	Neg.
RAW MATLS:	None	None	None
MANPOWER	Neg.	Neg.	Neg.
MAINTENANCE 6%			
CAPITAL RECOVERY 18%	10,000	21,200	39,800
MISC. CAP. COSTS 5%			
WASTE DISPOSAL	Neg.	Neg.	Neg.
RECOVERY CREDITS	300	800	2,400
VOC RECOVERED (MG/YR)	0.93	2.54	7.13
NET ANNUALIZED COST	9,700	20,400	37,400
COST EFFECTIVENESS ($/MG)	10,430	8,030	5,245

STORAGE & HANDLING, REFRIGERATED CONDENSING SYSTEMS

EVALUATION SHEET CASE NO. 2

	For 40 M Gal Tk	For 175 M Gal Tk	For 750 Gal Tk.
WASTE & RATE OF HDLG.			
DEC. 1979 INSTALLED CAPITAL COST	41,000	92,500	203,000
UTILITIES:			
Power @ $0.03/KWH	Neg.	Neg.	Neg.
RAW MATLS:	None	None	None
MANPOWER	Neg.	Neg.	Neg.
MAINTENANCE 6%			
CAPITAL RECOVERY 18%	11,900	26,800	58,900
MISC. CAP. COSTS 5%			
WASTE DISPOSAL	Neg	Neg	Neg
RECOVERY CREDITS	1,200	3,200	8,800
VOC RECOVERED (MG./YR)	3.53	9.56	26.53
NET ANNUALIZED COST	10,700	23,600	50,100
COST EFFECTIVENESS ($/MG)	3,031	2,470	1,890

STORAGE & HANDLING, REFRIGERATED CONDENSING SYSTEMS

EVALUATION SHEET   CASE NO. 3

	FOR 40 M Gal Tk	For 175 M Gal Tk	FOR 750 Gal Tk.
WASTE & RATE OF HDLG.			
DEC. 1979 INSTALLED CAPITAL COST	88,000	341,000	781,000
UTILITIES:			
Power @ $0.05/kWH	Neg	Neg	400
RAW MATLS:	None	None	None
MANPOWER	Neg.	Neg	Neg.
MAINTENANCE 6%			
CAPITAL RECOVERY 18%	25,500	98,900	226,500
MISC. CAP. COSTS 5%			
WASTE DISPOSAL	Neg	Neg.	Neg.
RECOVERY CREDITS	4,200	11,200	31,160
VOC RECOVERED (MG./YR)	12.58	33.94	93.91
NET ANNUALIZED COST	21,300	87,700	195,800
COST EFFECTIVENESS ($/MG)	1693	2585	2085

REPORT 2

FUGITIVE EMISSIONS

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Research Triangle Park, North Carolina

September 1980

D28I

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870 X 10^{-6}
Joule (J)	British thermal unit (Btu)	9.480 X 10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531 X 10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643 X 10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid/min) (gpm)	1.585 X 10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340 X 10^{-3}
Meter (m)	Inch (in.)	3.937 X 10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450 X 10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778 X 10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^{9}	1 Gg = 1 X 10^{9} grams
M	mega	10^{6}	1 Mg = 1 X 10^{6} grams
k	kilo	10^{3}	1 km = 1 X 10^{3} meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. CHARACTERIZATION AND DESCRIPTION

A. INTRODUCTION

The Synthetic Organic Chemicals Manufacturing Industry (SOCMI) is a segment of the domestic chemical industry that produces 378 basic and intermediate organic chemicals used to produce other intermediates and finished chemicals. Organic chemicals not included in the SOCMI are refinery by-products, coal-tar products, and other naturally derived organic chemicals or polymers.

For the purpose of this report fugitive emissions are defined as those volatile organic compound (VOC) emissions that result from leaking plant equipment. The potential sources of VOC emissions in the SOCMI that are considered in this report include pump seals, in-line (process and control) valves, relief valves, open-ended (sample, drain, vent) valves, compressor seals, flanges, and cooling towers. VOC emissions that result from the transfer, storage, treatment, and disposal of liquid, solid, and aqueous process wastes are defined as secondary emissions and are covered in a separate report[1].

The data base that was used for this report to characterize the industrial types of equipment was compiled from 53 plant site visits[2] and 2 EPA reports: Equipment Component Analysis for Identification of Potential Fugitive Emission Sources,[3] prepared by Pullman Kellogg, and Data Package for Formaldehyde Plant Fugitive Emissions Study,[4] prepared by Walk, Haydel and Associates, Inc.

The data supplied from the site visits and the two EPA reports include a quantification of the number of equipment components associated with a specific chemical or co-products manufactured from a specific process. The various equipment components, all of which are considered to be potential sources of fugitive emissions, were grouped into five major equipment categories: pumps, valves, compressor seals, flanges, and cooling towers. Pumps were further subdivided as to the type of seal used, with four subcategories considered: those with single mechanical seals, with double mechanical seals, with packed seals, or with no seals (sealless). Valves were subcategorized by type as saftey/relief, open-ended, and in-line, which were further subdivided by the kind of service as vapor (gas) or liquid.

B. SOURCES

There are many kinds of equipment in the SOCMI that can contribute VOC emissions from leakages. The types of equipment assessed for fugitive emissions in this report are as follows.

1. Pumps

Pumps are used extensively in the SOCMI for the movement of organic fluids. The predominant type used is the centrifugal pump, although other types, such as the positive-displacement pump, both reciprocating and rotary action, and the specialized canned and diaphragm pumps, are used for some applications. Except for such pumps as the canned and diaphragm types the pumps have a shaft that requires a seal to isolate the pump interior fluid from the atmosphere. The possibility of a leak through this seal makes it a potential source of fugitive VOC emissions.

The general types of shaft seals in use are packed, single mechanical, and double mechanical, which are listed in order of increased effectiveness in minimizing leaks. The sealless pump is, of course, the most effective. Proper installation and maintenance are required for all seal types if they are to function properly and retain their ability to seal.

a. Packed Seal——Figure II-1 is a diagram of a simple packed seal. Packed seals can be used on both reciprocating and rotary action types of pumps. The seal consists of a stuffing box in the pump casing filled with specialized packing material that is compressed with a packing gland to form a seal around the shaft. To prevent buildup of frictional heat, lubrication is required. A sufficient amount of either the liquid being pumped or the liquid that is injected must be allowed to flow between the packing and the shaft to provide the necessary lubrication.

b. Single Mechanical Seal——Figure II-2 is a diagram of a basic single mechanical seal. Mechanical seals can be used on rotary-type pumps only. The rotating-seal-ring face and the stationary-element face are lapped to a very high degree of flatness to ensure that they maintain contact throughout their mutual surface area. As with packing, the faces must be lubricated; however, because of their construction, much less lubrication is needed. There are many variations to

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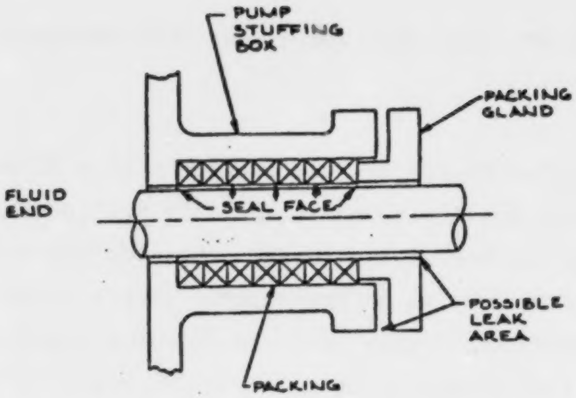


Fig. II-1. Diagram of a Simple Packed Seal

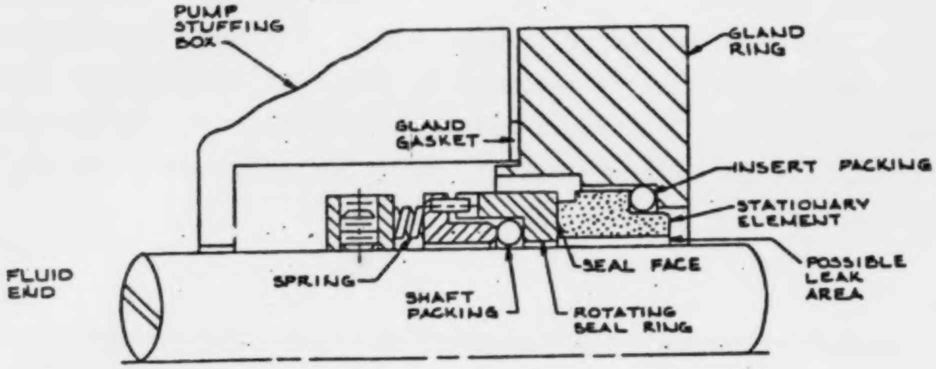


Fig. II-2. Diagram of a Basic Single Mechanical Seal

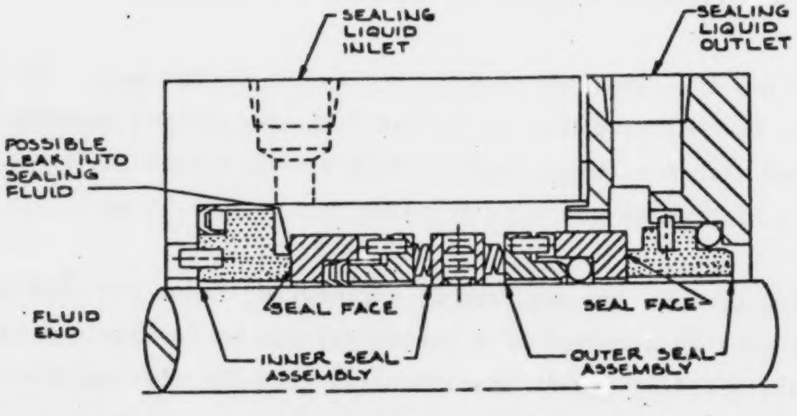


Fig. II-3. Diagram of a Double Mechanical Seal

the basic design but all have the lapped seal face between a stationary element and a rotating seal ring.

c. Double Mechanical Seal——Figure II-3 is a diagram of a double mechanical seal in which the two seals are installed in opposite configuration. A liquid, such as water or seal oil, is circulated through the stuffing-box space between the two seals. This arrangement is an improvement over a single seal since the sealing fluid surrounds the double seal and provides lubrication to both sets of seal faces. It also allows a low differential pressure to be set across the inner seal face.

Another double mechanical seal arrangement is one in which the two seals are installed in the same, or tandem, configuration. The inner seal functions identically to a conventional single inside seal. The stuffing box space between the two seals is flooded with a liquid from a closed reservoir. If the inner seal fails, it will be sensed by a pressure rise at the reservoir; also, the outer seal will take over as a backup seal.

2. Valves

One of the most common pieces of equipment in organic chemical plants is the valve. The types of valves commonly used are control, globe, gate, plug, ball, relief, and check valves. All except the relief valve and check valve are activated by a valve stem, whose motion may be rotational or linear or both, depending on the specific design. This stem requires a seal to isolate the valve interior fluid from the atmosphere. The possibility of a leak through this seal makes it a potential source of fugitive VOC emissions.

The most common type of valve stem seal in use is the packed seal. It consists of a stuffing box in the valve housing filled with specialized packing material that is compressed with a packing gland to form a seal around the stem. Figure II-4[5] is a diagram of one type of valve with a valve stem.

Pressure-relieving devices are required by engineering codes for applications in which the pressure on a vessel or a system may exceed the maximum allowed. Spring-loaded safety/relief valves are typically used for this service in the

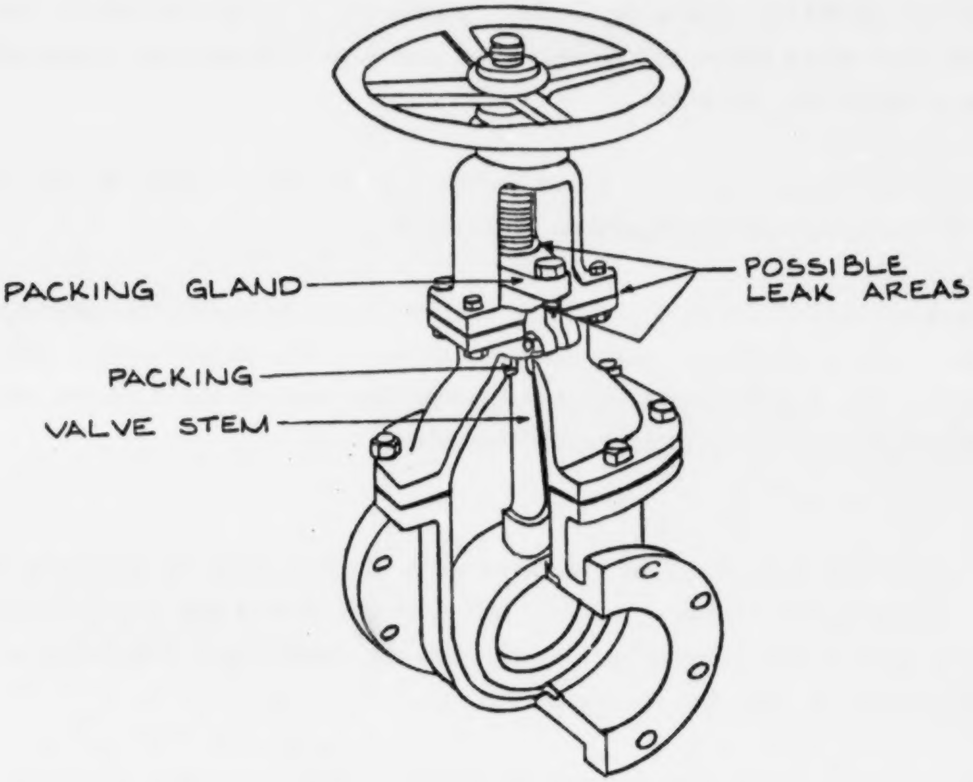


Fig. II-4. Diagram of a Gate Valve (from Ref. 4)

SOCMI. Figure II-5 is a diagram of a relief valve. The seal is a disk on a seat held in place by a spring during normal system operation. The possibility of a leak through this seal makes it a potential source of fugitive VOC emissions.

There are two potential causes for leaks: simmering, a condition due to the system pressure being close to the valve set pressure, and improper reseating following a relieving operation.

Check valves are used to prevent fluid backflow in a system. They do not need a seal and therefore are not a source of leakage.

Some valves are installed in a system so that they function with the downstream side open to the atmosphere. Examples are sample valves, drain valves, and vent valves. The possibility of a leak through the seat of these valves makes them a potential source of fugitive VOC emissions.

3. Flanges

Flanges are bolted gasket-sealed junctions used wherever pipe or equipment components such as vessels, pumps, valves, and heat exchangers may require isolation or removal. The possibility of a leak through the gasket seal makes them a potential source of fugitive VOC emissions.

Two primary causes of leakage are seal deformation due to thermal stress on the adjoining piping or equipment and repeated opening without replacement of the gasket.

4. Compressors

SOCMI compressors, like pumps, can be both centrifugal and positive-displacement types. Compressors have a shaft that requires a seal to isolate the compressor interior gas from the atmosphere. The possibility of a leak through this seal makes it a potential source of fugitive VOC emissions. In addition to having seal types like those for pumps, centrifugal compressors can be equipped with a liquid-film seal as shown in Fig. II-6.[6] The seal is a film of oil that flows between the rotating shaft and the stationary gland. The oil that leaves the compressor from the system side is under the system internal gas pressure and is contaminated with the gas. When this contaminated oil is returned to the oil reservoir, process gas can be released and emitted to the atmosphere.

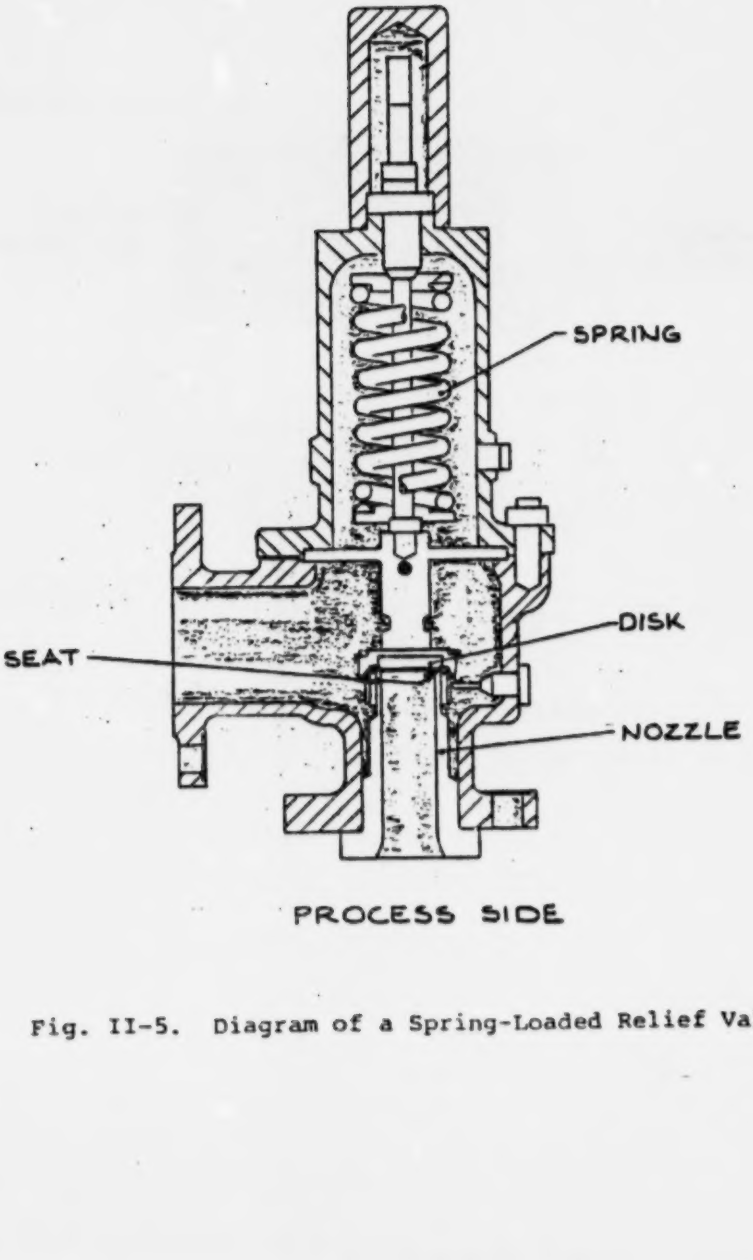
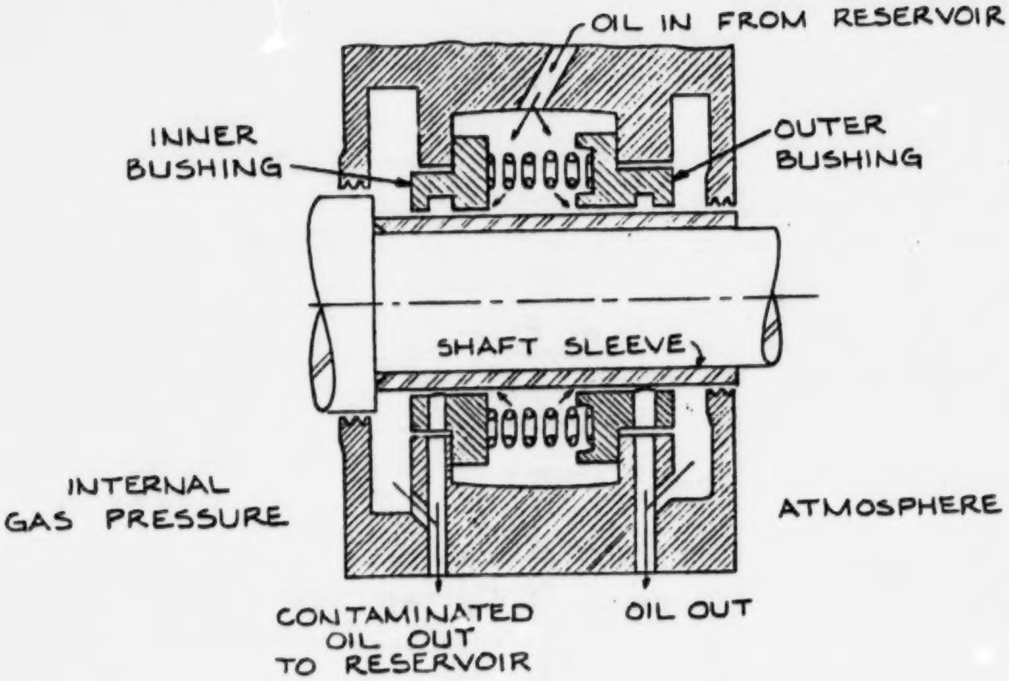


Fig. II-5. Diagram of a Spring-Loaded Relief Valve



128 Fig. II-6. Liquid-Film Compressor Shaft Seal (from Ref. 5)

5. Cooling Towers

Cooling towers cool the recirculating water that is used to remove heat from such process equipment as reactors, condensers, and heat exchangers. If a leak in the process equipment occurs and if the equipment is operating at a pressure higher than that of the recirculating water, process material can get into the water stream. This material can be released to the atmosphere at the cooling tower, making it a potential source of fugitive VOC emissions. A potential source of fugitive emissions can also occur if VOC-contaminated process water is used as the cooling-water source.

6. Other Sources

It is recognized that other kinds of equipment in the SOCMI can contribute VOC emissions from leakages that are not covered in this report; two of them are threaded connections and agitator seals. The use of threaded connections in VOC service is believed to be small, accounting for an estimated 2 to 3% of all piping-related connections.[3] Agitator seals could not be assessed for their fugitive emission potential because of insufficient data-base information.

C. METHODOLOGY

1. Data Base

The data base was compiled in the following two steps.

a. Step 1——In the first step all the equipment component data supplied by the reference sources for the valve and pump subcategories were averaged to yield a typical characterization for the industry. This approach was considered to be reasonable since the data represented both large- and small-capacity processes using both continuous- and batch-production operations. Results of the initial characterization of valves and pumps from the data base are given in Tables II-1 and II-2. This information is considered to be representative of the entire industry.

From Table II-1 it can be seen that safety and relief valves constitute 3.4% of the total valve population. An estimated 83% of the total safety-relief valves is in vapor service and 17% is in liquid service. Open-ended valves, which include sample, vent, and drain valves, represent 27.6% of the total valve count

Table II-1. SOCMI Valve Characterization[a]

Type of Valve	Percent of Total Valves	Percent in Liquid Service	Percent in Vapor (Gas) Service
Safety-relief	3.4	17.0	83.0
Open-ended (sample vent, drain)	27.6	91.0	9.0
In-line (process, control)[b]	69.0	65.0	35.0
All valves	100.0	71.0	29.0

[a] Includes only valves in VOC service.

[b] Check valves are excluded.

Table II-2. SOCMI Pump Seal Characterization[a]

Pump Seals	Percent in Use
Mechanical	
Single	71.9
Double	16.7
Packed	10.6
None (sealless)	0.8
Total	100.0

[a] Includes only pump seals in VOC service.

and are used primarily in liquid service (91%), with a small application (9%) in vapor service. In-line valves, including process and control valves, make up the bulk of the total valve population (69%) in the industry, with 65% of in liquid service and 35% in vapor service. In general, valves in the industry are used primarily in liquid service (71%), the remaining 29% being used in vapor service.

As is shown in Table II-2, the most common type of pump seal in use in the industry is the mechanical seal. An estimated 88.6% of all pump seals used to handle VOC are mechanical; 71.9% of them are single mechanical seals and 16.7% are double mechanical seals. Pumps with packed seals represent 10.6% of the total pumps. Less than 1.0% of the total industry pumps is sealless.

A basic assumption used in estimating the total SOCMI equipment components is that the total number of components associated with each chemical process is dictated more by the number of plants manufacturing the product than by the capacity of the production facility. A plant that is twice as large in capacity as another, producing the same chemical, does not necessarily have twice as many pieces of equipment. In most instances the equipment is simply larger in size. Plots that graphically illustrate the lack or correlation between the number of equipment components and a plant's rated capacity are shown in Appendix B. The plots were made for the total number of both pumps and valves versus the plant's rated capacity for selected sites in this data base.

Analysis of the data collected indicated that the plants in SOCMI varied considerably in size; i.e., the number of equipment components associated with one specific process differed by orders of magnitude from that associated with another. A second step in the data base compilation was therefore required to enable a scaleup.

b. Step 2——Three model plants were selected to represent existing small, medium, and large SOCMI plants. They are described in Table II-3. The most complete information obtained from the site visits and the two EPA reports was the total number of pumps at each location; therefore 15, 60, and 185 pumps were used to quantify small, medium, and large model plants respectively. Once the total number of pumps for each plant had been selected, the total number of valves

Table II-3. Equipment Data for Three Sizes of Model Plants

Equipment Component[b]	Number of Components in[a] Small Model Plant (A)	Medium Model Plant (B)	Large Model Plant (C)
Pump seals			
Light-liquid service			
Single mechanical	5	19	60
Double mechanical	3	10	31
Sealless	0	1	1
Heavy-liquid service			
Single mechanical	5	24	73
Packed	2	6	20
In-line valves			
Vapor service	90	365	1117
Light-liquid service	84	335	1037
Heavy-liquid service	84	335	1037
Safety-relief valves			
Vapor service	11	42	130
Light-liquid service	1	4	13
Heavy-liquid service	1	4	14
Open-ended valves[c]			
Vapor service	9	37	115
Light-liquid service	47	189	581
Heavy-liquid service	48	189	581
Compressor seals	1	2	8
Sampling connections[d]	26	104	320
Flanges	600	2400	7400
Cooling towers	1	1	1

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[a] 52% of existing plant units are similar to model-plant A; 33% are similar to model-plant B; 15% are similar to model-plant C.

[b] Includes equipment components in VOC service only.

[c] Sample, drain, purge valves.

[d] Based on 25% of open-ended valves.

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for each plant was calculated by using a valve-to-pump ratio of 25:1. This ratio is an average of the entire data base. A breakdown of the valves and pumps into the various types was completed based on the characterizations given in Tables II-1 and II-2.

It was assumed that pump seals are split 50/50 between light- and heavy-liquid service and that all packed pumps are used in heavy-liquid service, and all pumps with double mechanical seals are used in light-liquid service.[7] In-line valves, safety-relief valves and open-ended valves were assumed to be split 50/50 between light- and heavy-liquid service.[7] The heavy-liquid/light- liquid split was necessary because equipment components in heavy-liquid service have a lower leak frequency and smaller leak rates than equipment components in light-liquid service. A review of the data indicated a breakpoint between naphtha and kerosene. Heavy liquid, therefore, is defined as a fluid with vapor pressure equal to or less than 0.3 kPa at 20°C.

The total number of compressor seals for each of the three model plants was selected from the data base and is considered to be, in general, representative of SOCMI.

The total number of sampling connections in the model plants was estimated by assuming that 25% of the open-ended valves are in sampling service.[6] This percentage is considered to be representative of the data collected.

Flange estimates were made by developing a flange-to-valve ratio from the two EPA reports and the site visit information. A flange-to-valve ratio of 1.6:1, which reflects the use of welded and screwed valves and the existence of a significant number of open-ended valves, was considered to be representative of the data base.

Analysis of the data base indicated the use of normally one cooling tower per product site. Larger capacity operations usually had larger flow rates instead of additional cooling towers.

2. Industry Scaleup

A total of 1345 unique product units were identified with the production of the 378 organic chemicals that comprise SOCMI in 1978. A previous study[9] lists 2000 production units for SOCMI but when adjustments are made for the fact that some chemicals are co-produced in the same facility or are campaigned produced in a common facility, the number of actual or unique units reduces to 1345.

An analysis of the data base, with the total number of pumps used as the basis for selection, indicated that 52% of the SOCMI plant units would be classified as small, 33% would be classified as medium, and 15% classified as large.

The total industry estimate of equipment components was obtained by first multiplying the total number of SOCMI units (1345) by the estimated percentage of small, medium, and large plants. With this approach 700 plant units would be considered small, 445 plant units would be considered medium, and 200 plant units would be considered large. Then the average number of each of the specific equipment components for the three model plants was multiplied by the corresponding number of estimated units. The totals for each type of model plant were summed to yield a total estimate for SOCMI.

This extrapolation is considered to be valid because the data base consists of 62 plant units representing approximately 5% of the total SOCMI plant units and incorporates both large and small capacities and both batch- and continuous-production operations. The current total SOCMI equipment component estmate resulting from the scaleup is shown in Table II-4.

Table II-4. Current SOCMI Equipment Component Estimate

	Number of Components in			
Equipment Component[a]	Small Plants	Medium Plants	Large Plants	Total SOCMI
Pumps				
Light-liquid service				
Single mechanical seals	3,500	8,460	12,000	23,960
Double mechanical seals	2,100	4,450	6,200	12,750
Sealless	0	445	200	645
Heavy-liquid service				
Single mechanical seals	3,500	10,680	14,600	28,780
Packed seals	1,400	2,670	4,000	8,070
In-line valves				
Vapor service	63,000	162,430	223,400	448,830
Light-liquid service	58,800	149,080	207,400	415,280
Heavy-liquid service	58,800	149,080	207,400	415,280
Safety-relief valves				
Vapor service	7,700	18,690	26,000	52,390
Light-liquid service	700	1,780	2,600	5,080
Heavy-liquid service	700	1,780	2,800	5,280
Open-ended valves[b]				
Vapor service	6,300	16,470	23,000	45,770
Light-liquid service	32,900	84,100	116,200	233,200
Heavy-liquid service	33,600	84,100	116,200	233,900
Compressor seals	700	890	1,600	3,190
Sampling connections[c]	18,200	46,280	64,000	128,480
Flanges	420,000	1,068,000	1,480,000	2,968,000
Cooling towers	700	445	200	1,345
Agitators	d	d	d	d

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[a] Includes equipment components only in VOC service.

[b] Sample, drain, purge valves.

[c] Based on 25% of open-ended valves.

[d] No data available.

D. REFERENCES*

1. J. Cudahy and R. Standifer, IT Enviroscience, Inc., Secondary Emissions (June 1980) (EPA/ESED Report, Research Triangle Park, NC).

2. Site visits conducted and used to quantify various equipment components for the Fugitive Emissions report; see Appendix D.

3. Pullmann Kellogg, Houston, TX, Equipment Component Analysis for Identification of Potential Fugitive Emission Sources (data on file at EPA, ESED, Research Triangle Park, NC) (June 1978).

4. Walk, Haydel and Associates, Inc., New Orleans, LA, Data Package for Formaldehyde Plant Fugitive Emissions Study (data on file at EPA, ESED, Research Triangle Park, NC) (June 27, 1978).

5. Emissions from Leaking Valves, Flanges, Pump and Compressor Seals, and Other Equipment at Oil Refineries, LE-78-001, State of California Air Resources Board (April 1978).

6. R. F. Boland et al., Monsanto Research Corp., Screening Study for Miscellaneous Sources of Hydrocarbon Emissions in Petroleum Refineries, EPA-450/3-76-041 (December 1976).

7. Personal communication October 19, 1979, between K. C. Hustvedt, EPA, ESED, Research Triangle Park, NC, and D. Erikson, IT Enviroscience, Inc., Knoxville, TN

8. R. G. Wetherold et al., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, p 22, EPA Report No. 600/2-79-044 (February 1979).

9. Organic Chemical Producers' Data Base (OCPDB) Program, USEPA Cincinnati, OH, Updated November 28, 1979.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. EMISSIONS

A. INTRODUCTION

Data on the measurement of fugitive VOC emissions from SOCMI (synthetic organic chemical manufacturing industry) sources are limited. However, recent testing efforts have generated a considerable amount of information from petroleum refinery operations.[1] SOCMI fugitive VOC emissions are assumed to be very similar to petroleum refinery VOC emissions for all types of assessed sources. Data from petroleum refineries indicate that emission rates of sources decrease as the vapor pressure (volatility) of the process fluid decreases. Three classes of volatility have been established based on the petroleum refinery data: vapor service, light-liquid service, and heavy-liquid service. As noted in Sect. II, the split between light and heavy liquids for refinery data is between the streams of naphtha and kerosene. Table III-1[1] gives the uncontrolled fugitive VOC emission factors that resulted from testing conducted at petroleum refineries and that have been applied to SOCMI equipment components to generate VOC fugitive emission estimates.[1]

All pumps in light-liquid service, except for sealless pumps, have an uncontrolled emission factor of 0.12 kg/hr. It was assumed that pumps with double mechanical seals leak VOC through the inner seal at the same rate as single mechanical and packed seals and that the VOC is emitted from the seal-oil degassing vent. All pumps in heavy-liquid service, except for sealless pumps, also have the same uncontrolled emission factor of 0.02 kg/hr based on the same assumptions stated above.

Uncontrolled emission factors for all the remaining sources were obtained directly from the refinery study.[1,2]

Cooling towers were not assessed for emissions because data from petroleum refineries indicate that cooling towers are a very small source of VOC fugitive emissions. Differences in SOCMI operating procedures, such as recirculation of process water, might result in cooling-tower VOC fugitive emissions but no data are available to verify this.

Table III-1. Uncontrolled Fugitive Emission Factors for the SOCMI

Fugitive-Emission Source	Uncontrolled Emission Factor (kg/hr)[a]
Pumps	
Light liquids	
With packed seals	0.12
With single mechanical seals	0.12
With double mechanical seals	0.12[b]
With no seals	0.0
Heavy liquids	
With packed seals	0.020
With single mechanical seals	0.020
With double mechanical seals	0.020[b]
With no seals	0.0
Valves (in-line)	
Gas	0.021
Light liquid	0.010
Heavy liquid	0.0003
Safety-relief valves	
Gas	0.16
Light liquid	0.006
Heavy liquid	0.009
Open-ended valves	
Gas	0.025
Light liquid	0.014
Heavy liquid	0.003
Flanges	0.0003
Sampling connections	0.015
Compressors	0.44
Cooling towers	c
Agitators	c

[a] These uncontrolled emission levels are based upon the refinery data presented in ref 1.

[b] Assumes that the inner seal leaks at the same rate as single seal and that the VOC is emitted from the seal-oil degassing vent.

[c] No data available.

Agitators also were not assessed for VOC fugitive emissions because the number of agitator seals in SOCMI in not known. Furthermore the emission rate from SOCMI agitator seals has not yet been measured. Since there are no data on similar sources in other industries, no estimates of the emission rate were available. Because of these uncertainties, cooling towers and agitator seals are not included in the model plant or industry emission estimates.

B. FUGITIVE-EMISSIONS ESTIMATES

SOCMI VOC fugitive emissions are presented in two ways: uncontrolled emissions have been calculated for each of the three model plants described in Table II-3, and uncontrolled emissions have been calculated for the entire industry based on the industry scaleup and resulting equipment component estimate given in Table II-4.

Uncontrolled VOC fugitive emission estimates for the small, medium, and large model plants described in Sect. II are given in Table III-2. Emission estimates were calculated by multiplying the equipment components in Table II-3 by the emission factors in Table III-1.

Uncontrolled VOC fugitive emissions that were estimated for SOCMI are shown in Table III-3. The total emissions are currently estimated to be 321,000 Mg annually, which accounts for approximately 40% of the total VOC emissions from SOCMI in 1980.

The largest source of VOC fugitive emissions are valves in vapor service that contributed a total of 166,000 Mg of VOC emissions, or 52% of the total estimated VOC fugitive emissions resulting from SOCMI.

Table III-2. Fugitive Emission Estimates for Three Model Plants

Equipment Component[a]	Uncontrolled VOC Emissions (kg/yr) in Small Model Plant	Medium Model Plant	Large Model Plant
Pumps			
Light-liquid service			
Single mechanical seals	5,256	19,973	63,072
Double mechanical seals	3,154	10,512	32,587
Sealless	0	0	0
Heavy-liquid service			
Single mechanical seals	876	4,205	12,790
Packed seals	350	1,051	3,504
In-line valves			
Vapor service	16,556	67,145	205,483
Light-liquid service	7,358	29,346	90,841
Heavy-liquid service	221	880	2,725
Safety-relief valves			
Vapor service	15,418	58,867	182,208
Light-liquid service	53	210	683
Heavy-liquid service	79	315	1,104
Open-ended valves			
Vapor service	1,971	8,103	25,185
Light-liquid service	5,764	23,179	71,254
Heavy-liquid service	1,261	4,967	15,269
Compressor seals	3,854	7,709	30,835
Sampling connections	3,416	13,666	42,048
Flanges	1,577	6,307	19,447
Total	67,164	256,435	799,035

[a] Equipment in VOC service only.

Table III-3. Current SOCMI Uncontrolled Fugitive-Emissions Estimate

Fugitive-Emission Source[a]	Uncontrolled Emissions[b] (Mg/yr)
Pumps	
Light-liquid service	
Single mechanical seals	25,187
Double mechanical seals	13,403
Sealless	0
Heavy-liquid service	
Single mechanical seals	5,042
Packed seals	1,414
In-line valves	
Vapor service	82,567
Light-liquid service	36,379
Heavy-liquid service	1,091
Safety-relief valves	
Vapor service	73,430
Light-liquid service	267
Heavy-liquid service	416
Open-ended valves	
Vapor service	10,024
Light-liquid service	28,600
Heavy-liquid service	6,147
Compressor seals	12,296
Sampling connections	16,882
Flanges	7,800
Cooling towers	c
Agitators	c
Total	320,945

[a] Includes sources in VOC service only.

[b] Based on emission factors listed in Table III-1.

[c] Not estimated; no data available.

C. REFERENCES

1. R. G. Wetherold *et al*., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, p 22, EPA Report No. 600/2-79-044 (February 1979).

2. The Assessment of Environmental Emissions from Oil Refining, Appendix B, Vol 3, EPA Report No. 600/2-80-075C (April 1980).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. CONTROL TECHNOLOGY

This section describes the existing technology for the control of fugitive emissions in the synthetic organic chemicals manufacturing industry (SOCMI). The control of equipment leaks (fugitive emissions) can be accomplished not only by the installation of control devices but also by the use of monitoring (leak detection) and maintenance procedures.

A. CONTROL DEVICES

In some cases the equipment can be modified to limit VOC emissions from SOCMI plants. The modifications included in this report that are considered to be control devices consist of double mechanical seals on pumps, rupture disks and a closed-vent system for safety/relief valves, blinds and a closed-loop sampling system for open-ended valves, and a closed-vent system for compressor liquid-film seals.

1. Double Mechanical Seals

Double mechanical seals can be superior to single mechanical seals and packed seals in preventing leakage from rotary-type pumps and compressors. By design double mechanical seals have a chamber between the two seal faces that is either flushed with a sealing fluid that allows control of the conditions under which the seal operates or that flooded with a fluid whose pressure can be monitored for seal failure.

Any leaks through the inner seal may be dissolved or suspended in the sealing fluid, and subsequent degassing of the sealing fluid may result in the emission of VOC. Therefore sealing-fluid degassing vents must be controlled in order to provide maximum control effectiveness of double mechanical seals. After extended periods of use double mechanical seals may also develop leaks at the outer-seal shaft junction.

Emissions of VOC from degassing vents can be controlled by a closed-vent system, which consists of piping and, if necessary, flow-inducing devices to transport the degassing emissions to a control device such as a flare, a process heater, or a vapor-recovery system. Control effectiveness as high as 99% for a double mechanical seal and closed-vent system is possible depending on the effectiveness of the auxiliary control device and on the frequency of mechanical seal failure. Failure of both the inner and outer seals can result in relatively large VOC emissions at the seal area of the pump. As noted, the pressure monitoring of the sealing fluid may be used to detect failure of the seals. In addition, visual observation of the seal area can be effective in detecting failure of the outer seal.

Mechanical seals, single or double, are limited in their applications. They can be used only on shafts with a rotary motion. Also, the maximum service temperature is usually limited to less than 260°C.[1] Despite their limitations it is estimated that about 90% of the SOCMI pumps handling VOC are equipped with mechanical seals, with 17% being double mechanical seals (Sect. II). Therefore double mechanical seals could be used in most new-pump applications and probably could be retrofitted to replace many of the present single mechanical seals and some of the packed seals. When the VOC being handled by the pump has a low vapor pressure, the emission potential is reduced, which could limit the necessity for double mechanical seals in these applications.

2. Rupture Disks

A rupture disk can be installed upstream of a relief valve in order to prevent fugitive emissions through the relief-valve seat.[2] Figure IV-1 is a diagram of a rupture-disk and relief-valve installation. Under normal conditions the rupture disk seals the system tightly, but if its set pressure is exceeded, it will break, at which time the relief valve will relieve the pressure. This procedure may require the use of a larger size relief valve because of operating codes. The disk/valve combination may also require appropriate piping changes to prevent disk fragments from lodging in the valve and precluding it from being reseated should the disk rupture. A block valve upstream of the rupture disk is also required in order to permit in-service replacement of the disk after rupture. If the disk were not replaced, the first overpressure would result in the relief valve being the same as an uncontrolled relief valve, and it may actually be worse since disk fragments may prevent proper reseating of the relief valve. In some chemical plants installation of a block valve upstream of a pressure-relief device may be common practice. In others it may be forbidden by operating or safety procedures. Tandem pressure-relief devices with a three-way valve can be used to prevent operation without relief protection.

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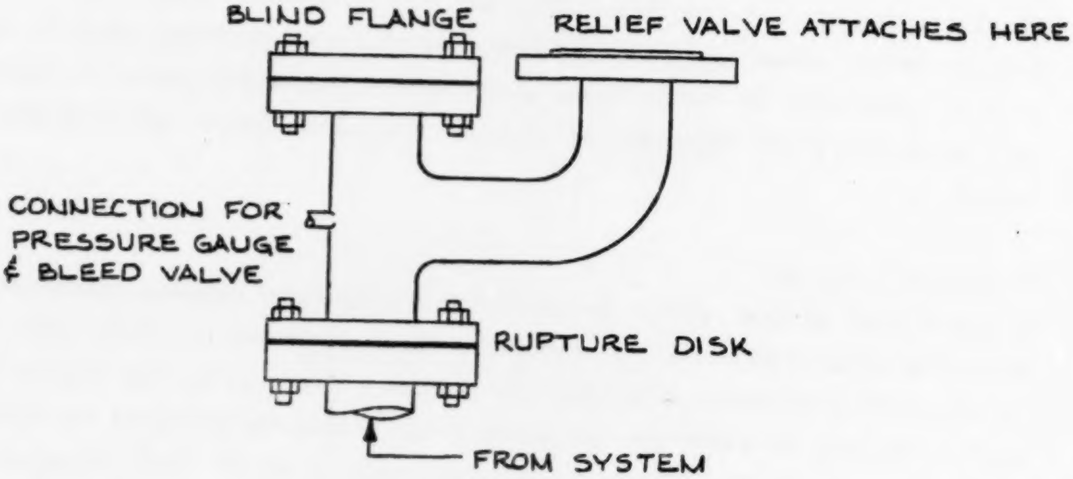

Fig. IV-1. Diagram of a Rupture Disk Installation Upstream of a Relief Valve

In rupture-disk/relief-valve combinations there must be some provision for testing the integrity of the disk. It is important that no pressure be allowed to build up in the pocket between the disk and the relief valve; otherwise the disk will not function properly. The pocket must be connected to a pressure indicator, recorder, or alarm. If the process fluid is not hazardous or toxic, a simple bubbler apparatus could be used to test the integrity of the disk by connection of the bubbler to the pocket. The control efficiency of the disk/valve combination is assumed to be 100% for fugitive emissions resulting from improper seating and from simmering of the relief valve. If the disk integrity is not maintained or if the disk is not replaced after rupture, the control efficiency would be lowered. The disk/valve combination has no effect on emissions resulting from over-pressure relieving.

Manufacturers of relief valves state that resilient-seat or O-ring relief valves provide better reseating qualities compared to standard relief valves. No test data are available to verify these statements. These improvements would have no effect on rupture emissions or fugitive emissions due to seal failure or simmering.

3. Closed-Vent System

A closed-vent system is used to collect and dispose of gaseous emissions in many industrial operations, particularly those processes in which large volumes of combustible volatile materials are handled. These gases can result from such conditions as plant upsets, which require that the material be vented to prevent overpressuring from plant startups and shutdowns, from disposal of waste-gas streams, and from equipment leaks. Such emissions are typically intermittent, and their flow rates during major upsets can be large. The usual method of disposing of them is by flaring. Figure IV-2 is a diagram of a dual-flare system. The small flare operates more efficiently with routine smaller exhausts. The large flare is normally on standby to handle large emergency exhausts.

By connecting relief-valve discharges and compressor seal-oil degassing vents to a closed-vent system, their emissions can be effectively controlled. The effectiveness of VOC destruction will depend on the flare design and turn-down capability. A dual-flare system should be more effective than a single-flare system for the relatively low flows from relief-valve leaks and compressor seal-oil degassing.

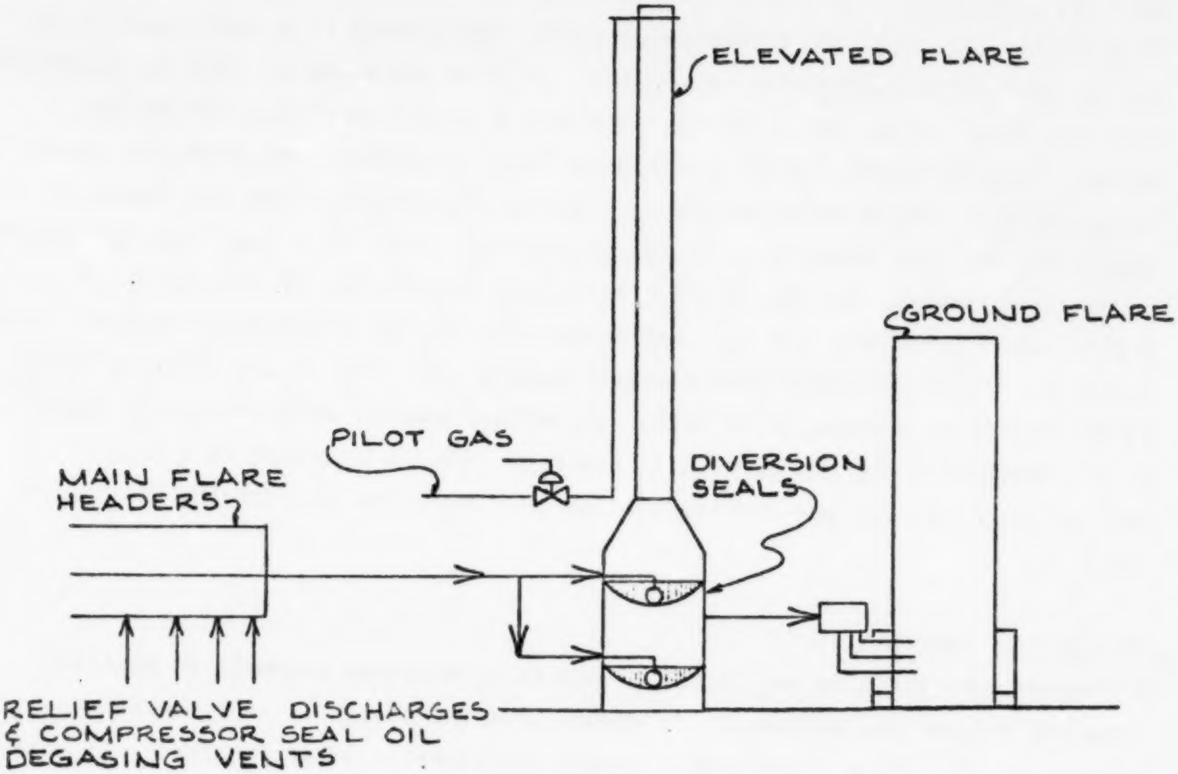

Fig. IV-2. Diagram of Simplified Closed Vent System With Dual Flares

4. Blinds, Caps, and Plugs

Blinds, caps, plugs, or a second valve are devices for closing off the ends of valves and pipes. When installed downstream of an open-ended valve, they are effective in preventing leaks through the seat of the valve from reaching the atmosphere. Open-ended valves in SOCMI, about 28% of the total valves handling VOC, are used mostly in intermittent service for sampling, venting, or draining. If a blind, cap, plug, or second valve is used downstream of a valve when it is not in use, VOC emissions can be reduced. If a second valve is used in conjunction with the first valve, the upstream valve should always be closed before the second valve is closed. A further modification to minimize VOC emissions would be to install a bleed valve between the two valves (double block and bleed) to remove any VOC that might have leaked through the first valve and then accumulated in the area between the two valves. Each time that the blind, cap, plug, or second valve is opened, any VOC that leaked through the first valve will be released. These emissions have not been quantified. The control efficiency of these devices is assumed to be 100%. The actual control efficiency will depend on how frequently the cap or plug is removed. The installation of a blind, cap, or plug does not prevent the leakage that may occur through the valve-stem seal.

5. Closed-Loop Sampling

A frequent operation in many SOCMI plants is to withdraw a sample of material from the process for analysis. To ensure that the sample is representative, purging of the sample lines and/or sample container is often required. If this purging is done to the atmosphere or to open drains and if there are incidental handling losses, VOC emissions can result. A closed-loop sampling system is designed so that the purged VOC is returned to the system or sent to a closed disposal system and so that the handling losses are minimized. Figure IV-3[3] shows two examples of closed-loop sampling systems, in which the purged VOC is flushed from a point of higher pressure to one of lower pressure in the system and where sample-line dead space is minimized. Reduction of emissions from the use of closed-loop sampling is dependent on the efficiency of the control device to which the purge is directed, i.e., 99% for a flare or 100% if the purge is returned to the process. Flare efficiencies have not veen satisfactorily documented except for specific designs and operating conditions using specific fuels. An efficiency of 99% was used for tentative comparison purposes.

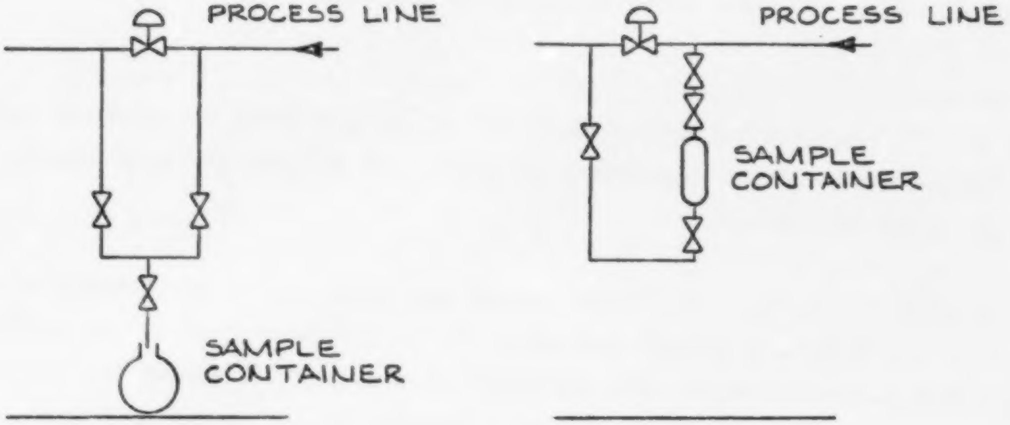

Fig. IV-3. Diagram of Two Closed-Loop Sampling Systems (from Ref. 5)

B. LEAK DETECTION METHODS (MONITORING)

The EPA has defined a leak as one having a VOC concentration of over 10,000 ppm at the potential leak source.[4] The emission rate predicted by linear regression analysis for 10,000 ppm at 0 cm is 0.42 kg/day for pump seals and 4.5 kg/day for gas valves.[5]

Leak detection can be accomplished by three types of monitoring: individual-component survey, unit-area survey, and multiple fixed-point monitoring systems. Monitoring methods, their advantages and disadvantages, and their leak detection efficiencies are discussed. The leak detection efficiency is defined as the number of leaks detected by the monitoring method on a given date divided by the total number of leaks known to exist on that same date.

1. Individual-Component Survey[6]

Each type of equipment listed in Sect. II can be monitored for leaks by use of a portable VOC detection instrument to sample the ambient air in proximity to the potential leak point.

In a complete individual-component survey each leak source is screened by a portable VOC detection device that measures the concentration at the surfaces where leakage could occur. The instrument probe should traverse the length of the leak interface at the leak surface. Some potential sources, such as process drains, cooling towers, pressure-relief devices, and open-ended valves or pipes, have an exhaust area open to the atmosphere rather than a seal interface. For these sources the probe should be placed at the centroid of the open area, as well as around the perimeter of the open area. The major advantage of the complete individual-component survey is that all significant equipment leaks are located. By checking each component individually at its surface there should be no false indicating leaks that are emenating from another leak source.

2. Unit Area Survey[6]

A unit area survey entails measuring the ambient VOC concentration within a given distance, for example, 1 m, of all equipment located on the ground and other accessible levels within a processing area. These measurements are performed with a portable VOC detection instrument utilizing a strip-chart recorder. The instrument operator walks a predetermined path to assure total available coverage of a unit on both the upwind and downwind sides of the equipment, noting on the chart record the location in the unit where any elevated VOC concentrations are detected. If an elevated VOC concentration is recorded, the components in that area would be screened individually to locate the specific leaking equipment. It is estimated that 50% of all leaks in the unit are detected by the walk-through survey, provided that all major leaking equipment has been repaired, which reduces the VOC background concentration sufficiently to allow for reliable detection.[7]

The major advantages of the unit-area survey are that leaks from ground and other accessible leak sources can be located quickly and that the manpower requirements are much lower than those for the individual-component survey. Some of the shortcomings of this method are that VOC emissions from adjacent units can cause false leak indications; high or intermittent winds (local meteorological conditions) can increase dispersion of VOC, causing leaks to go undetected; and additional effort is necessary to locate the specific leaking equipment. However, two or more consecutive (back-to-back) surveys in a unit would minimize these problems.

3. Fixed-Point Monitoring Systems[6]

The basic concept of the fixed-point monitoring system is that sampling-point devices can be installed at specific sites within the process area to monitor for leaks automatically. The ambient VOC concentration can be remotely and centrally indicated to the operator, who can respond appropriately when elevated levels are recorded. The monitoring sites would not include the entire geographic area of the facility, but only those areas where equipment handling VOC is located. The performance of individual equipment can also be monitored to detect equipment failures that result in leaks.

The approaches to leak detection with fixed-point monitors differ in the number and placement of the sample points and in the manner in which the sample is taken and analyzed. One approach is to establish the sample points near specific pieces of equipment, such as process pumps, compressors, and cooling towers. Another approach is to establish the sample points in a grid pattern throughout the process area. When an elevated concentration is noted, the operator makes an individual-component survey on equipment in that area to locate the leaking component. In addition to these variations in the location of the sampling points, different types of systems can be used. For example, the sampling can be done continuously and the analysis done on-site or the samples can be collected at the site and then be analyzed at a central location (an automatic sequential system).

One feature of the fixed-point monitor approach is that the location of the monitor and the type of sampling and analysis can be tailored to meet the specific requirements of individual plant sites and VOC. Fixed-point monitors can sample for specific compounds by flame ionization—gas chromatography (GC/FID) or infrared (IR) analysis. Of the several leak detection methods, fixed-point monitoring systems have the highest capital cost but the lowest manpower requirement for monitoring. However, this approach may still require the use of a portable VOC detection device to locate the leak, particularly if process-area monitoring is used. Leak detection efficiency for fixed-point monitoring systems is estimated to be 33%[6] for facilities with a small number of recurring leaks, provided that major leaking equipment has been repaired, which reduces the VOC background concentration sufficiently to allow for reliable detection.

4. Cooling-Tower Total Organic Carbon (TOC) Analyzer

If there is a leak into a cooling-water system, detection by a portable or fixed-point monitor may not be possible at the cooling tower. The air in close proximity to the tower is normally very turbulent as the result of wind drafts created by operation of the tower. This can increase the dispersion of VOC and cause the leak to go undetected. To overcome this problem, a TOC analyzer can be used to monitor for total organic carbon (ppm) in the cooling-tower stream. At one plant using such a system a difference in total carbon measurements of ≥5 ppm between inlet and outlet cooling-water streams at the tower is considered to be an indication of a leak.[8] Samples are then taken from various individual items of equipment that make up the cooling-water system until the leak is found. The leak detection efficiency for TOC monitoring of cooling water with concentrations ≥5 ppm is expected to be high.

5. Visual Inspection

Visual inspections can be performed to detect evidence of liquid leakage from plant equipment. Any liquid leak found on equipment in VOC service should be repaired because it represents equipment not operating properly and it represents a potential release of VOC to the atmosphere.

C. MAINTENANCE

When leaks are located by the monitoring methods described in this section, the leaking component must be repaired or replaced. Many components can be serviced on-line, which is generally regarded as routine maintenance to keep operating equipment functioning properly. Equipment failure, as indicated by a leak not eliminated by servicing, requires isolation of the faulty equipment for either repair or replacement.

1. Pumps

Most critical-service process pumps in SOCMI are backed up with a spare in place so that they can be isolated for repair. Of those pumps that are not backed up with spares, most can be isolated without major process disruption. Packed-seal leaks frequently can be corrected by just tightening the packing, whereas mechanical-seal leaks and packed-seal leaks that need correction require that the pump be removed from service for seal repair. When the seal leak is small, there can be situations in which the temporary emissions resulting from removal of the pump from service can be larger than the emissions that would occur if the pump remained in service until shut down for other process reasons. The maintenance lead time required to schedule repair of a leaking pump can be an important factor in the VOC emission-reduction efficiency obtainable.

2. Valves

Most valve leaks can probably be corrected on-line by tightening the packing gland for valves with packed seals or by lubrication for plug valves, for example. Based on field observation in one refinery study[9] it was assumed that 75% of leaking valves could be repaired on-line. Leaking valves that need to be repacked or to be removed for repair must be capable of being isolated or the unit must be completely or partly shut down. Control valves, 6% of the total valves in SOCMI, can usually be isolated.[1] Block valves, which are used to isolate or by-pass equipment, normally cannot be isolated. One refiner estimates that 10% of the block valves can be isolated.[1] Based on the assumption that there is a random distribution of leaks versus valve type and usage, in about 3% of the leaks the valve can be isolated and in 22% the unit will have to be shut down for repair of the valve.

When the leaking valves can be corrected on-line, repair servicing is usually done soon after the leak is detected. For leaks that can be corrected by isolation of the valve the maintenance lead time required to schedule repair can be an important factor in the VOC emission-reduction efficiency obtainable. When the leaks can be corrected only by a total or partial unit shutdown, the temporary emissions could very likely be larger than the continuous emissions that would result from not shutting down the unit until it was time for a shutdown for other reasons.

3. Flanges

In one refinery field study it was noted that flange leaks could be sealed effectively on-line by simply tightening the flange bolts.[9] For a flange leak that requires off-line gasket seal replacement a total or partial shutdown of the unit would probably be required because most flanges cannot be isolated. For many of these cases there are temporary flange repair methods that can be used. Unless a leak is major and cannot be temporarily corrected, the emissions resulting from the shutting down of the unit would probably be larger than the continuous emissions that would result from not shutting down the unit until time for a shutdown for other reasons. Flange leak incidences are very low and most can be corrected by on-line maintenance.

4. Compressors

Compressors usually are in critical service and most often a spare is not provided. In most cases shutdown for repair of a leaking seal and the subsequent startup will involve flaring the process stream until operations are stablized.[2] This can result in shutdown emissions being larger than the continuous emissions that would occur until it was time for the unit to be shut down for other reasons.

D. REFERENCES*

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3. Briggs, T. and V. P J. Patel, Evaluation of Emissions from Benzene-Related Petroleum Processing Operations EPA Report No. 450/3-79-022 (October 1978).

4. EPA, Chemical and Petroleum Branch, OAQPS Guideline Series, Control of Volatile Organic Compound Leaks from Petroleum Refinery Equipment, EPA-450/2-78-036, OAQPS No. 1.2-111 (June 1978).

5. R. G. Wetherold *et al*., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, p 22, EPA Report No. 600/2-79-044 (February 1979).

6. K. C. Hustvedt and R. C. Weber, Detection of Volatile Organic Compound Emissions from Equipment Leaks, paper presented at 71st Annual Air Pollution Control Association Meeting, Houston, TX, June 25—30, 1978.

7. R. C. Weber,EPA, personal communications with D. G. Erikson, IT Enviroscience, Inc., Oct. 26, 1978 (analysis of preliminary results of EPA test program).

8. J. F. Lawson, IT Enviroscience, Inc., Trip Report for Visit to Union Carbide Corp., South Charleston, WV, Dec. 7, 1977 (data on file at EPA, ESED, Research Triangle Park, NC).

9. Emissions from Leaking Valves, Flanges, Pump and Compressor Seals, and Other Equipment at Oil Refineries, LE-78-001, State of California Air Resource Board (Apr. 24, 1978).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

V. COST ANALYSIS

This section presents estimated costs for the control of VOC fugitive emissions from equipment leaks in the synthetic organic chemicals industry (SOCMI).

A. INTRODUCTION

Estimates of capital and annual operating costs are given for controlling emissions from equipment leaks at SOCMI plants. The major sources of VOC emissions that are considered in this section include pump and compressor seals, in-line valves, open-ended valves, safety-relief valves, flanges, and cooling towers. Control costs are presented for the five equipment modifications discussed in Sect. IV. They include the installation of double mechanical seals, installation of a rupture disk before a safety-relief valve, capping open-ended valves, sampling by the closed-loop method, and incorporating a compressor-degassing vent and safety-relief vents into an existing closed-vent system. Control costs are also developed for a one-time-only leak detection program for the three model plants decribed in Sect. II.

Plants in the SOCMI vary considerably in the size, configuration, and age of facilities, the products produced, and the degree of control. Because of the variations among plants this cost analysis is based on the three model plants described in Sect. II and on the equipment data given in Table V-1. As was stated earlier, the parameters considered to be representative of existing small, medium, and large SOCMI plants are from the data base compiled for this report. It is estimated that 15% of the SOCMI plants would be considered to be large, 33% to be medium, and 52% to be small. Although model plant costs may differ, sometimes appreciably, from the actual costs that may be incurred, they are the most useful means from determining and comparing emission control costs.

B. CONTROL COSTS

Capital cost estimates represent the investment required to purchase and install monitoring instruments for leak detection and the labor and material costs to install each of the five equipment modifications.

Table V-1. Equipment Data for Three Model Plants

Equipment Component[b]	Number of Components in[a] Small Model Plant	 Medium Model Plant	 Large Model Plant
Pump seals			
Light-liquid service			
Single mechanical	5	19	60
Double mechanical	3	10	31
Sealless	0	1	1
Heavy-liquid service			
Single mechanical	5	24	73
Packed	2	6	20
In-line valves			
Vapor service	90	365	1117
Light-liquid service	84	335	1037
Heavy-liquid service	84	335	1037
Safety-relief valves			
Vapor service	11	42	130
Light-liquid service	1	4	13
Heavy-liquid service	1	4	14
Open-ended valves[c]			
Vapor service	9	37	115
Light-liquid service	47	189	581
Heavy-liquid service	48	189	581
Compressor seals	1	2	8
Sampling connections[d]	26	104	320
Flanges	600	2400	7400
Cooling towers	1	1	1

[a] 52% of existing plant units are similar to Model Plant A. 33% of existing plant units are similar to Model Plant B. 15% of existing plant units are similar to Model Plant C.

[b] Includes equipment components only in VOC service.

[c] Sample, drain, purge valves.

[d] Based on 25% of open-ended valves.

1. Control Devices (Equipment Modifications)

Details of the capital cost estimates for the five equipment modifications are given in Appendix C. The cost factors used in computing annual operating costs for all five equipment modifications are shown in Table V-2. In computing the depreciation and interest costs, a capital recovery factor of 0.163 was used based on a 10-yr life at an interest rate of 10% per annum. Costs for property taxes and insurance are computed at 4% of the capital costs. All operating costs are for 1-year periods, beginning with the first quarter of 1979. Table V-3 shows the installed capital cost per unit for each of the five equipment modifications. Costs for loss of production during installation or startup, preparation of the equipment for retrofitting, or other highly variable costs are not included in the estimates.

a. Double Mechanical Seals——The installed cost for retrofitting a single mechanical seal or a packed seal is estimated to be $850.[1—3] This cost consists of $560 for the seal and $290 labor for field installation. The installed cost for a new double mechanical seal is estimated to be $575. A credit of $225[1—3] for a new single mechanical seal was subtracted from the double-seal cost of $560 to yield a net double-seal cost of $335. Labor to install the new double mechanical seal in a shop area was estimated at $240. Actual costs for double mechanical seals will range from $400 to $2000, depending on the pump shaft diameter, the material of construction of the seal, the pump operating pressure and temperature, and the physical and chemical properties of the material to be pumped. Auxiliary equipment, such as a cooler for control of the temperature of the liquid used to flush the seal, may be required and can range in cost from $470 to $800;[1] also, an individualized pressurized-pot system may be required to maintain pressure on the liquid used to flush each double seal and can cost from $400 to $700.[1,3]

b. Rupture Disks

The cost for a rupture disk located upstream of a relief valve is estimated to be $1730 for a new installation and $3110 for a retrofitted installation. One 7.6-cm carbon-steel rupture-disk holder costs $324.[4,5] One 7.6-cm stainless-steel rupture disk costs $195.[4,5] One 0.6-cm dial-face pressure gauge costs $15. One 0.6-cm carbon-steel bleed valve gate costs $25. The installation cost for installation of these items is $240. In order to allow in-service disk replacement, a block valve must be installed upstream of the rupture disk

Table V-2. Cost Factors Used in Computing Annual Costs for Equipment Modifications (Control Devices)[a]

Maintenance	0.05 X capital cost
Capital charges	
Capital recovery	0.163 X capital cost
Miscellaneous (taxes, insurance, and administration)	0.04 X capital cost

[a] These cost factors are different than those that are used in other IT Enviroscience reports but were used to be consistant with EPA's proposed standard documents.

Table V-3. Cost Estimates for Installation of Control Devices in Model Plants

Control Device	Unit Cost
Double mechanical seals	
New	$ 575
Retrofitted	$ 850
Flush oil system for double mechanical seals, per pump	$1500
Rupture disks for relief valves	
New	$1730
Retrofitted	$3110
Caps for open-ended valve)	$ 45
Closed-loop sampling connections	$ 460
Closed vents for degassing reservoirs of compressors and double-seal pumps	
Compressor	$6530
Pumps	$3265

at an installed cost of $760. In order to prevent disk fragments from damaging the relief valve, an off-set mounting, which consists of one 10.2-cm tee and one 10.2-cm elbow at an installed cost of $140, is required. Cost for the retrofit installation is based on the assumption that a new relief valve is required to replace the existing de-rated relief valve and that there is no credit for the used (replaced) relief valve. Installed cost for a 7.6-cm pressure-relief valve is estimated to be $1380.

Actual costs for just the rupture disks can range from $200 to $1200 depending on the operating pressure required, the number of disks purchased, the material of construction required, and the size of the disk itself. The rupture disk can become a cost-saving installation if it allows the relief valve to be tested in place instead of having to be removed to a shop area. This is normally done once or twice annually.

c. Caps on Open-Ended Valves——The installed cost of a blind flange on an open-ended valve is estimated to be $30. This cost includes the blind flange and the bolt and gasket set and is representative of either a new or retrofitted installation. Actual costs for blinding or plugging open-ended valves could range from $20 to $200 depending on whether a plug, cap, or blind flange is used, on the size of the valve, and on the material of construction required.

The installed cost for a 2.5-cm screwed valve is estimated to be $45. Purchase cost is estimated to be $30 with $15 required for 1-hr installation.

d. Closed-Loop Sampling——The cost of a closed-loop sampling system is estimated to be $460 for either a new or a retrofitted installation. The costs are based on a 6-m length of 2.5-cm-diam, schedule 40, carbon-steel pipe and three 2.5-cm-diam carbon-steel ball valves. It is estimated from the data base that approximately 25% of the open-ended valves are used for sampling. Actual costs will be highly variable, depending on pipe size and material of construction required. For example, the use of type 316 stainless steel pipe would increase installation costs for the above system to $828.

e. Closed-Vent System——The installation of a vent line from the compressor oil-seal reservoir and from the plant safety relief valves to an existing (retrofitted) controlled closed-vent system is estimated to be $6530.[6] This cost is based on the installation of a 122-m length of 5.1-cm-diam, schedule 40, carbon-steel pipe at a cost of $5200 and on three 5.1-cm-diam cast-steel plug valves and one 5.1-cm-diam metal gauze flame arrestor at a cost of $1330. It is estimated that only one vent line with a header system is necessary for collecting the vapors. A cost of $3265 for double mechanical seal pumps is based on the assumption that two pumps (such as a pump and its spare) are connected to a single degassing vent. Actual costs will depend on the line size required, the locations of relief valves and compressor reservoirs, and the materials of construction. If a controlled closed-vent system is not in place, the installation costs will be significantly higher.

2. Leak Detection and Maintenance

The manpower required to monitor equipment leaks varies with the methods or combination of methods used. The manpower required for monitoring has been estimated for each of the three model plants discussed in Sect. II. These estimates are based on an industry estimates[7], and the monitoring guidelines discussed in Sect. IV. Table V-4 shows the maximum number of leaks measuring >10,000 ppm at the leak surface available for detection per year for each of the three model plants.[1,8]

Table V-5 shows the annual manpower (man-hours) required at each model plant for monitoring an individual-component survey one time with a portable organic analyzer.[6] Two analyzers are used for example cost, one for use and one as a spare. Flanges are not monitored since the leak occurrence is considered to be negligible. For the purposes of these estimates only, it is assumed that this survey will be conducted by two people: one operating the portable VOC detection instrument and the other recording the results.

It will be noted that no matter what leak detection method is used, associated maintenance manpower will be required for repairing the leaking component. These requirements (shown in Table V-6) are estimated from an EPA report[6] and from the assumptions noted in the table. The actual maintenance manpower required is directly proportional to the percentage of leaks detected; i.e., if only one-half the leaks are detected, then the maintenance man-hours will be 50% of those shown in Table V-6.

Table V-4. Basis for Determining Monitoring/Maintenance Manpower Requirements

	Number of Sources[a]	Percentage of Initial Leaks[b]	Number of Leaks Detected[c]
	Small Model Plant		
Pumps (light liquid)			
Single mechanical	5	23	2
Double mechanical	3	23	1
In-line valves			
Vapor	90	10	9
Light liquid	84	12	11
Safety-relief valves (vapor)	11	8	1
Open-ended valves[d]			
Vapor	9	10	1
Light liquid	47	12	6
Compressor seals	1	33	1
	Medium Model Plant		
Pumps			
Single mechanical	19	23	5
Double mechanical	10	23	3
In-line valves			
Vapor	365	10	37
Light liquid	335	12	41
Safety-relief valves (vapor)	42	8	3
Open-ended valves[d]			
Vapor	37	10	4
Light liquid	189	12	23
Compressor seals	2	33	1
	Large Model Plant		
Pumps			
Single mechanical	60	23	14
Double mechanical	31	23	8
In-line valves			
Vapor	1117	10	112
Light liquid	1037	12	125

Table V-4. (Continued)

	Number of Sources[a]	Percentage of Initial Leaks[b]	Number of Leaks Detected[c]
Safety-relief valve (vapor)	130	8	0
Open-ended valves[d]			
Vapor	115	10	12
Light liquid	581	12	70
Compressor seals	8	33	3

[a] From data base.

[b] See ref 9.

[c] All leaks ($\geq$10,000 ppm) assumed to be detected.

[d] Refers to the valve and not the open end.

Table V-5. Annual Monitoring Manpower Requirements for Individual-Component Survey for Three Model Plants

Components	No. of Components per Model Plant[a]			Type of Monitoring	Estimated Time for Monitoring[b] (min)	Times Monitored (No./yr)[b]	Annual Manpower Required (hr) per Model Plant[c]		
	Small	Medium	Large				Small	Medium	Large
Pump seals	15	60	185	Instrument	5	1	2.5	10	30.8
Compressor seals	1	2	8	Instrument	10	1	0.3	0.7	2.7
In-line valves (gas)	90	365	1117	Instrument	1	1	3.0	12.2	37.2
In-line valves (liquid)	168	670	2074	Instrument	1	1	5.6	22	69.1
Open-ended valves[d]	104	415	1277	Instrument	1	1	3.5	14	42.6
Safety-relief valves	13	50	157	Instrument	8	1	3.5	13.3	41.9
Pipeline flanges	600	2400	7400	None					
Total							18.4	72.2	224.3

[a] From report data base.

[b] See ref 6.

[c] Except where otherwise noted, based on 2 persons required.

[d] Refers to valve and not open end.

Table V-6. Maintenance Manpower vs Requirements for Initial Leak Repair for Three Model Plants

Source Type	Components Per Model Plant			Number of Initial Leaks			Repair Time (hr)	Labor-Hours Required		
	Small Plant	Medium Plant	Large Plant	Small Plant	Medium Plant	Large Plant		Small Plant	Medium Plant	Large Plant
Pumps (light liquid)										
Single mechanical	5	19	60	2	5	14	80	160	400	1120
Double mechanical	3	10	31	1	3	8	80	80	240	640
Valves (in-line)										
Vapor	90	365	1117	9	37	112	1.13	10	42	127
Light liquid	84	335	1037	11	41	125	1.13	12	46	141
Safety-relief valves										
Vapor	11	42	130	0[a]	0[a]	0[a]	0	0	0	0
Open-ended valves										
Vapor	9	37	115	1	4	12	1.13	1	5	14
Light liquid	47	189	581	6	23	70	1.13	7	26	79
Compressor seals	1	2	8	1	1	3	40	40	40	120
Total								310	799	2241

[a] No maintenance required because rupture disks are assumed in use.

The cost factors used to compute annual operating cost for leak detection are shown in Table V-7.[6,9] These factors are based on an EPA report and on engineering estimates. In computing the depreciation and interest costs, a capital recovery factor of 0.163 was used based on a 10-year life at an interest rate of 10% per annum for the fixed-point monitoring system. A capital recovery factor of 0.23 was used, based on a 6-yr life at an interest rate of 10% per annum, for the portable VOC analyzers. Costs for property taxes and insurance are computed at 4% of the capital costs. All operating costs are for 1-year periods, beginning with the first quarter of 1979. Tables V-8 and V-9 show the installed capital cost, the annual instrument capital-related costs, the annual instrument materials, the maintenance and calibration costs, and the total annual operating costs for each of the three model plants.

The installed capital cost for the instruments shown in Table V-8 is $8500, based on the use of two portable organic analyzers (one used as a spare) at a cost of $4250 each.[6] The annual cost for instrument materials, maintenance, and calibration is $2700,[6] including replacement of one battery pack and two filter packs per year. The annual monitoring and maintenance costs are shown in Table V-9. The annual monitoring labor cost for each model plant was obtained by multiplying the total monitoring manpower requirements by $15/hr.[6] The annual maintenance labor cost for each model plant was obtained by multiplying the total maintenance manpower requirements by $15/hr.[6]

The installed instrument capital cost shown in Table V-10 is $136,000, which includes $8,500 for two portable VOC analyzers and $127,500[9] for a 20-point gas-chromatograph fixed-point monitor. The annual instrument capital-related cost of $28,500 consists of $2,600 for the portable analyzers and $25,900 for the fixed-point unit. Annual instrument materials, maintenance, and calibration costs of $9100 reflect a cost of $2700 for the portable analyzer and $6400 for the fixed-point monitor.

Table V-7. Factors Used in Computing Annual Costs for Monitoring Systems

Monitoring-instrument capital	
Portable	\$4250[a]
Fixed point (installed)	\$127,500[b]
Labor	
Monitoring	\$15.00/hr[a]
Maintenance	\$15.00/hr[a]
Annual instrument capital-related cost	
Capital recovery	
Portable monitor	0.23 X capital
Fixed-point monitor	0.168 X capital
Miscellaneous (taxes and insurance)	0.04 X capital
Annual instrument material, maintenance, and calibrations	
Portable monitor	\$2700[a]
Fixed-point monitor	0.05 X capital cost
Annual administrative and support	0.4 X annual monitoring and maintenance cost[a]

[a] From ref 6.

[b] From ref 9.

Table V-8. Control Cost Estimate for Leak Detection for Three Model Plants

	Cost for Small, Medium, and Large Model Plant
Instrument installed capital	$8,500
Annual instrument, capital-related	2,600
Annual instrument materials maintenance and calibration	2,700
Total	$5,300

Table V-9. Annual Monitoring and Maintenance Costs for Leak Detection for Three Model Plants

	Cost for		
	Small Model Plant	Medium Model Plant	Large Model Plant
Annual monitoring labor	$ 280	$ 1,090	$ 3,370
Annual maintenance labor	4,650	11,980	33,620
Annual administrative and support	1,970	5,230	14,800
Total	$6,900	$18,310	$51,790

Table V-10. Control Cost Estimates for a Fixed-Point Monitoring System with an Individual-Component Survey

	Cost for Small, Medium, and Large Model Plant
Instrument capital	$136,000
Annual instrument, capital-related	$28,500
Annual instrument material maintenance and calibration	9,100
Total	$ 37,000

C. REFERENCES*

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5. E. Wischhusen, Knoxville, TN, representative of BS&B Safety Systems, Inc., personal communication Jan. 22, 1979, with D. G. Erikson, IT Enviroscience, Inc. (documented for files of D. G. Erikson).

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9. K. C. Hustvedt and R. C. Weber, *Detection of Volatile Organic Compound Emissions from Equipment Leaks*, paper presented at 71st Annual Air Pollution Control Association Meeting, Houston, TX, June 25—30, 1978.

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VI. ASSESSMENT

A. SUMMARY

Fugitive emissions are VOC emissions that result from leaks from plant equipment. Equipment characterized in this report includes pump seals, in-line valves, open- ended valves, safety-relief valves, compressor seals, flanges, and cooling towers. The total estimate of equipment components in VOC service in the SOCMI includes 72,200 pumps, 1,855,000 valves, 2,968,000 flanges, 3,190 compressors, and 1,345 cooling towers. It is estimated that 50% of the above equipment components are used in light-liquid service and 50% are used in heavy-liquid service. The uncontrolled fugitive emission factors listed in Table III-1 and used throughout this report are based on operating conditions found to exist in the petroleum industry in 1978. If it is assumed that the SOCMI operates with the same degree of equipment maintenance and monitoring, the estimated fugitive emissions from the total SOCMI may be as high as 320,945 Mg/yr. The actual degree of maintenance and monitoring control used in the SOCMI has not been established. Control of fugitive VOC emissions is primarily achieved by use of leak detection and maintenance methods. They range from a complete testing of every potential VOC leak source to the use of fixed-point monitors installed to detect leaks in specific process unit areas. Leak detection efficiencies range from 100 to 33%. A significant leak is defined as one that is >10,000 ppm read out on a portable VOC analyzer at the source of the leak (0-cm distance). In addition to leak monitoring and maintenance, five specific equipment modifications can be used as a supplement to eliminate VOC emissions specific to those sources.

Installed capital costs range from $45 to $3,110 for each equipment modification and from $8,500 to $136,000 for leak detection methods.

APPENDIX A

TOTAL NUMBER OF SOCMI PRODUCT SITE LOCATIONS

Table A-1. Total Number of SOCMI Product Unit Locations[a]

Location	Number of Product Units[b]
Texas	220
New Jersey	140
Louisiana	95
Illinois	90
Ohio	77
California	75
Pennsylvania	71
New York	64
West Virginia	37
Tennessee	32
Alabama	32
North Carolina	32
Kentucky	30
Indiana	28
Michigan	25
Puerto Rico	23
All others	271
Total	1345

[a] Organic Chemical Producers Data Base (OCPDB) Program, USEPA Cincinnati, OH, Updated Nov. 28, 1979.

[b] A product unit is defined as a geographic location that utilizes specific pieces of equipment to produce one or more specific synthetic organic chemicals.

APPENDIX B

CHARACTERIZATION OF MODEL PLANTS AND NUMBER OF PUMPS AND VALVES VERSUS PLANT CAPACITY

Table B-1. Model Plants Characterized to Date[a]

Plant Type	Total Number of Components in[b]				Plant Capacity (Gg/yr)
	Pumps	Process Valves	Relief Valves	Compressors	
Acrylic acid and esters	36	820	44		76.1
Acrylonitrile	50	1200			180
Adipic acid	56	349	22		150
Chlorobenzenes	102	800	12		96
Chloromethanes	30	1000	15	2	45—180
Cyclohexane-benzene	15	300	15	1	30—265
Cyclohexane-petroleum	35	700	35	1	100
Cyclohexanol/cyclohexanone via cyclohexane	75	1975	56		100
Cyclohexanol/cyclohexanone via phenol	35	875	26		100
Ethylbenzene/styrene	50	1000			300
Ethylene	165	4150	65	8	408.2—680.3
Ethylene dichloride	42	1100	40		400
Ethylene oxide via air	10	400		2	227
Ethylene oxide via oxygen	10	400		2	136.1
Formaldehyde	13	214	6		45
Maleic anhydride	15	500			22.7
Nitrobenzene	42	500	20		30—150

---

[a] From Emissions Control Options for the Synthetic Organic Chemicals Manufacturing Industry——Product Reports (on file at EPA, ESED, Research Triangle Park, NC).

[b] In VOC service only.

Log Y = .82 + .27 Log X (Slope)

r^2 = 0.07 (Correlation Coefficient)

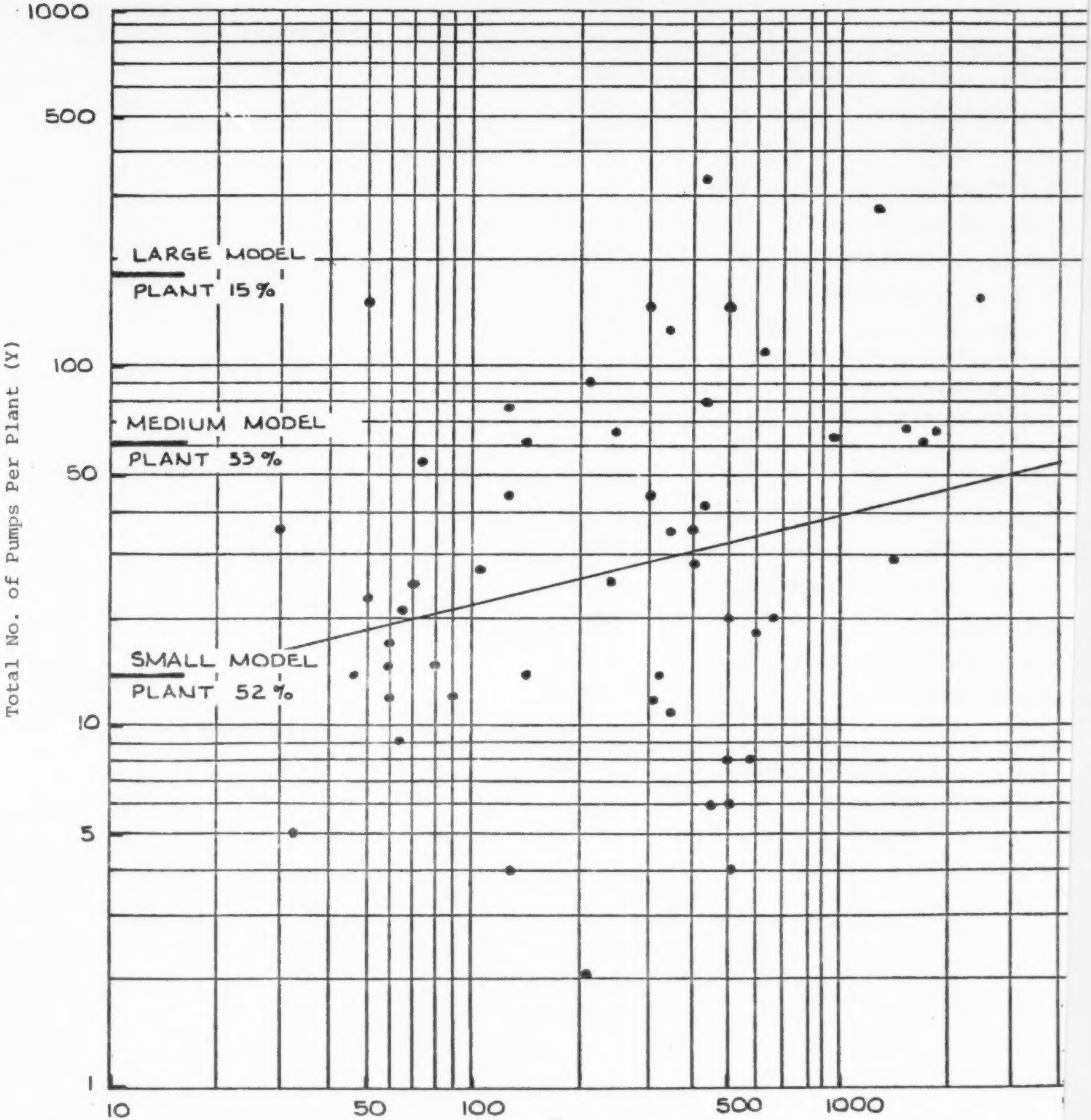

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Fig. B-1 . Total Number of Pumps for Each Plant in the Data Base Versus the Plant's Rated Capacity (54 Points)

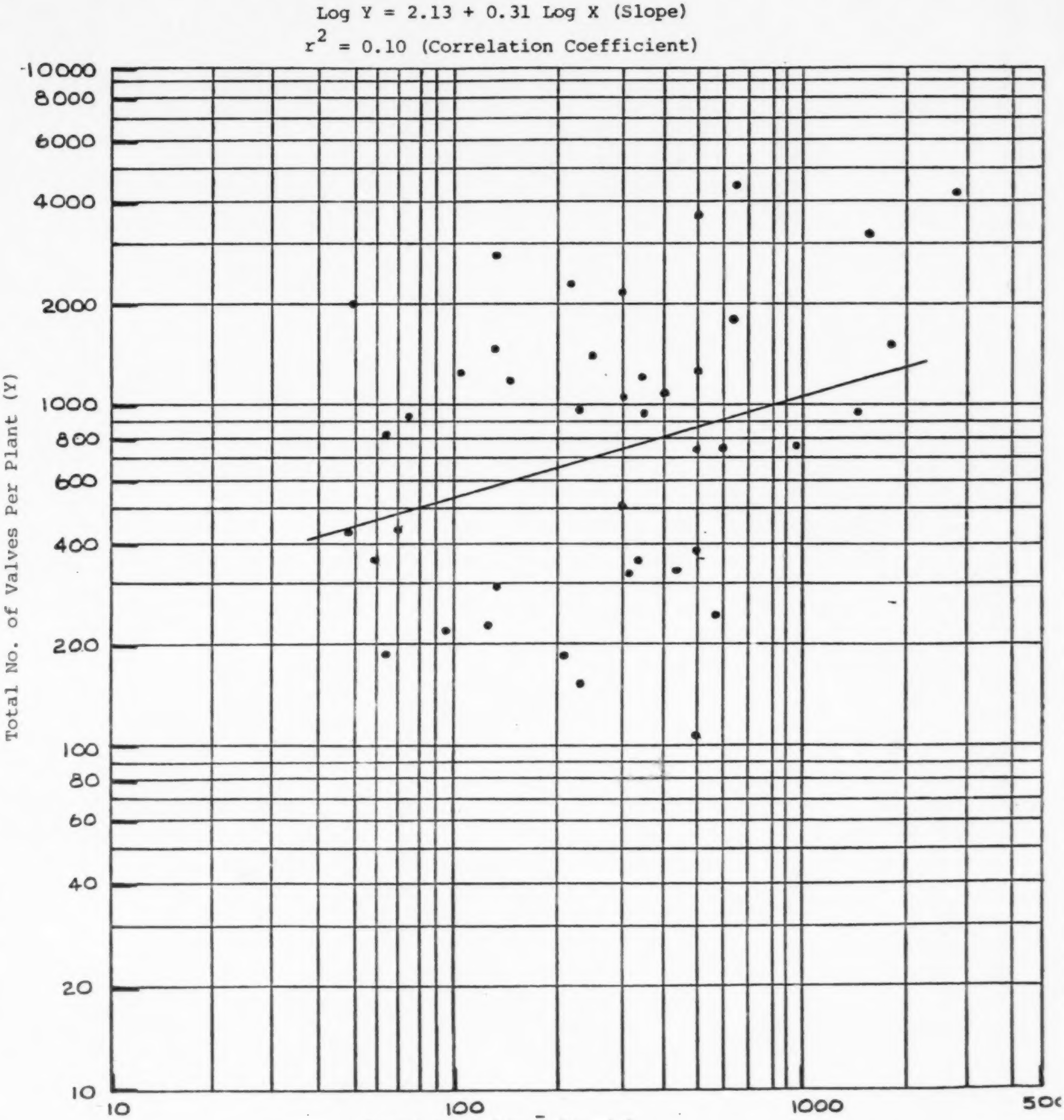

Fig. B-2. Total Number of Valves for Each Plant in the Data Base Versus the Plant's Rated Capacity (42 Points)

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APPENDIX C

COST ESTIMATE DETAILS

PRELIMINARY CAPITAL

SHEET ___ OF ___

PROJECT: Double mechanical Seals - New and Retrofit

PHASE:

E F NUMBER:

BY: D.G. Erikson

DATE: Jan. 22, 1979

JOB NUMBER: 9101-F

CASE NUMBER:

SECTION NUMBER:

SECTOR NUMBER & NAME:

	NAME OF FACILITY / DESCRIPTION / QUANT.		
(1.)	Single Mechanical Seal 1 3/4" shaft Ceramic vs carbon faces 316 S.S Construction (Material only)		$225 00
(2)	Double mechanical seal 1 3/4" shaft, balanced, 316 SS Construction installed new		$800.00
(3)	Double mechanical seal as above retrofit		$850

PRELIMINARY CAPITAL C-4 [illegible]

SHEET 0

PROJECT Rupture Disk below Safety Relief valve

PHASE	E F NUMBER	BY	DATE	JOB NUMBER
		D.G Erikson	Jan. 22, 1979	9101-F

CASE NUMBER	SECTION NUMBER	SECTOR NUMBER & NAME

	NAME OF FACILITY | DESCRIPTION | QUANT.		
1	Rupture disk 1000 PSIG MAX in nickel, aluminum or 316 Stainless 3" ave SIZE Φ		195.00
2	Rupture disk holder Carbon steel set within 2"-4" bolt circle 3" AVE SIZE Φ		375.00
3.	Pressure gauge 2½" Φ dial face ¼" Connection		15.10
4.	½" Bleed valve gate 150 # rising stem Carbon steel		24.45
	Total		609.5
			$610.0

PRELIMINARY CAPITAL

SHEET OF

PROJECT Blinds on open-ended values

DATE JAN. 22, 1979

JOB NUMBER 9101-F

PHASE

E F NUMBER

BY D.C. ERIKSON

CASE NUMBER

SECTION NUMBER

SECTOR NUMBER & NAME

	NAME OF FACILITY DESCRIPTION QUANT.		
1	Blind flange 150# Carbon		
	steel 60% 1" values		
	40% 4" values		
			11.93
1	Gasket set 1/16" Rasied face stud		
	Bolt AND 1/16" Compressed		
	Asbesto ring GASKET		
	60% 1" values 4: 4" values		$17.96
			$29.89
	Total		
			30.00

PRELIMINARY CAPITAL C-6

SHEET

PROJECT: Closed Loop Sampling System

PHASE:

E F NUMBER:

BY: D.G. Erikson

DATE: Jan. 23, 1979

JOB NUMBER: 9101-F

CASE NUMBER:

SECTION NUMBER:

SECTOR NUMBER & NAME:

	NAME OF FACILITY DESCRIPTION QUANT.		
1	Piping		
	Sample Line 20' x 1" Φ		
	Carbon Steel sch. 40		$ 145.00
2	3- 1" Φ ball values carbon		
	steel construction		164.40
	total		$ 309.40
			use $ 31

PRELIMINARY CAPITAL

SHEET OF

PROJECT: Closed Vent System Fugitive Emissions

PHASE:

E F NUMBER:

BY: D.G Erikson

DATE: Jan. 23, 1979

JOB NUMBER: 9101-F

CASE NUMBER:

SECTION NUMBER:

SECTOR NUMBER & NAME:

	NAME OF FACILITY / DESCRIPTION / QUANT.		
1.	Piping		
	Vent 2" Φ x 400' LG		
	Carbon steel		$5200
2.	Plug type valves (3)		
	2" Φ Cast steel		
			$900
3.	Flame Arrestor, fine metal gauze		
	type 2" Φ		$430
Total	Installed cost 79'		$6530

APPENDIX D

LIST OF EPA INFORMATION SOURCES

LIST OF EPA INFORMATION SOURCES*

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REPORT 3

SECONDARY EMISSIONS REPORT

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Research Triangle Park, North Carolina

June 1980

D73A

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870 X 10^{-6}
Joule (J)	British thermal unit (Btu)	9.480 X 10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531 X 10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643 X 10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585 X 10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340 X 10^{-3}
Meter (m)	Inch (in.)	3.937 X 10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450 X 10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778 X 10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^{9}	1 Gg = 1 X 10^{9} grams
M	mega	10^{6}	1 Mg = 1 X 10^{6} grams
k	kilo	10^{3}	1 km = 1 X 10^{3} meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. THE SOCMI WASTES

A. INTRODUCTION

The synthetic organic chemical manufacturing industry (SOCMI), which produces an estimated 350 to 400 chemicals by approximately 600 processes, generates large quantities and a wide variety of wastes. Secondary emissions, as used in this report, are defined as emissions of volatile organic compounds (VOC) that result from the handling, treatment, and disposal of aqueous, liquid, and solid wastes generated by the industry. Organic emissions from cooling towers are considered as fugitive emissions and are discussed in a separate report.[1] Emissions that result from the treatment or control of process emissions are not considered as secondary emissions unless they emanate from aqueous, liquid, or solid wastes generated in the treatment or control of process emissions.

B. PROCESS WASTE SOURCES

1. Introduction

An overview of typical waste sources and the probable characteristics of wastes from each type of source is given in Table II-1. It should be emphasized that only the more prevalent combinations of sources and types of wastes are included. The major waste categories shown include aqueous wastes, liquid organic wastes, and solid wastes (including sludges and slurries). The major waste categories are further subdivided according to probable characteristics [i.e., content of organics, inorganics, water, solids, metal salts, and acids or bases (pH)] that may influence or restrict treatment or disposal techniques and, in turn, affect the resulting secondary emissions.

Table II-2 summarizes the primary operations that generate wastes and the corresponding types of wastes for 34 of the most significant chemicals produced by the SOCMI and for 41 of the primary processes used. Although the products listed account for less than 10% of the total number of chemicals produced, they account for more than 70% of total industry production and total industry VOC emissions. A number of the processes listed, however, do not generate significant secondary emissions. The data in Table II-2 were extracted from Emissions Control Options for the SOCMI: Product Reports, which are incorporated in other volumes of this report, and cover the products listed in the first column.

Table II-1. Summary of Common Process Waste Sources and Corresponding Waste Characteristics

	Aqueous							Liquid Organic				Solids Slurries and Sludges			
	Organic Conc.														
Process Waste Sources	Trace—1000ppm	1000—10,000 ppm	>10,000 ppm	Contains Dissolved Inorganics	Contains Suspended Solids	Basic pH, >10	Acidic pH, <4	Organics Only	Contains Dissolved Inorganics	Contains Suspended Solids	Contains Water	Contains Organics Only	Contains Inorganics	Contains Heavy Metals	Contains Water
Distillation															
Overhead															
Conventional drying	x	x	x												
Azeotropic drying	x	x	x												
Bottoms															
Conventional								x	x	x	x	x	x	x	x
Steam stripping	x	x		x	x	x	x								
Steam distillation		x	x	x	x	x	x	x	x	x	x	x	x	x	x
Water contact operations	x	x	x	x	x	x	x								
Reaction															
Process water	x	x	x	x	x	x	x								
Nonaqueous by-products								x	x	x	x	x	x	x	x
Spent catalyst													x	x	x
Off-grade products								x				x			
Gas compression/vacuum generation															
Rotary devices	x	x	x					x			x	x			
Venturi devices	x	x	x	x	x	x									
Liquid/liquid phase separation	x	x	x	x	x										
Solid/liquid separation															
Sedimentation															
Liquid phase	x	x	x	x	x			x	x	x	x				
Solid phase												x	x	x	x
Filtration															
Filter cake												x	x	x	x
Wash water	x	x		x	x										
Adsorption															
Adsorbent												x	x	x	
Process water	x	x		x											
Storage															
Settled water	x	x	x	x	x										
Settled sludge												x	x	x	x
Process area															
Leaks, washdown	x	x	x	x	x										
Cleanouts	x	x	x	x	x			x	x	x	x	x	x	x	x
Spills								x	x	x	x				

Table II-2. Waste Sources in Selected SOCMI Processes

Product	Primary Process	Estimated 1978 Production (Gg/yr)[a]	Type of Waste	Waste Source
Acetaldehyde	Ethylene oxidation	450	Aqueous	Distillation bottoms
			Liquid	Distillation side cut
Acetone/phenol	Cumene	900	Aqueous	Water scrubbing, phase separation, distillation bottoms
Acetic anhydride	Acetic acid pyrolysis	680	Aqueous	Gas scrubbing, vacuum steam-jet ejector
			Solid	Distillation bottoms, sludge evaporator
Acrylic acid and esters	Propylene oxidation	410	Aqueous	Quench-absorber, distillation
			Spent sulfuric acid	Distillation
			Liquid	Distillation
			Solid	Distillation, spent catalyst
Acrylonitrile	Propylene ammoxidation	815	Aqueous	Distillation, steam stripping
			Liquid	Distillation
Adipic acid	Nitric acid oxidation	855	Aqueous	Deep-well holding pond
Alkylbenzene	Olefins	250	Aqueous	HF scrubber, azeotropic distillation, vacuum jet
			Solids	Calcium fluoride from HF scrubber

Table II-2. (Continued)

Product	Primary Process	Estimated 1978 Production (Gg/yr)^a	Type of Waste	Waste Source
	Chlorination		Aqueous	Distillation, phase separation, neutralization, steam jets
			Liquid	Phase separation (skimming)
			Solid	Catalyst sludge spent filters
Butadiene	n-Butane dehydrogenation	260	Aqueous	Distillation, phase separation
			Solid	Polymeric residues from solvent and product purification
	Oxidative dehydrogenation	265	Aqueous	Distillation, phase separation, steam condensed in quench tower
			Solid	Polymeric residues from solvent and product purification
	By-product of ethylene manufacture	975	Aqueous	Distillation, phase separation
			Solid	Polymeric residues from solvent and product purification
Caprolactam	Cyclohexanone	400	Aqueous	Neutralization, distillation, filtration
			Liquid	Neutralization, distillation bottoms
		220	Aqueous	Caustic scrubber, heavy-

Table II-2. (Continued)

Product	Primary Process	Estimated 1978 Production (Gg/yr)[a]	Type of Waste	Waste Source
Chloromethanes	Methane chlorination	930	Aqueous	Spent sulfuric acid, waste caustic from scrubbers, misc. wastewater
			Liquid	Distillation residues
Cumene	Phosphoric acid catalyst	968	Aqueous	Phase separation
			Solid	Spent catalyst
	Aluminum chloride catalyst	289	Aqueous	Azeotrope distillation, phase separation, scrubbers
Cyclohexanol/cyclohexanone	Cyclohexane	1,012	Aqueous	Stripper overhead, misc. sources
			Liquid	Distillation residues
	Phenol hydrogenation	178	Liquid	Catalyst reactivation
Ethanolamines	Ethylene oxide and ammonia	165	Aqueous	Steam jet condensate
			Liquid	Distillation residues
Ethylene	Ethane/propane feed	6,100	Aqueous	Quench effluent phase separation
			Solid	Pyrolysis coke
	Naphtha feed	3,000	Aqueous	Quench effluent phase separation
			Solid	Pyrolysis coke

Table II-2. (Continued)

Product	Primary Process	Estimated 1978 Production (Gg/yr)[a]	Type of Waste	Waste Source
	Gas oil feed	3,000	Aqueous	Quench effluent, phase separation
			Solid	Pyrolysis coke
Ethylbenzene/styrene	Benzene alkylation/ dehydrogenation	3,220	Aqueous	Aluminum chloride catalyst solution, spent caustic
			Liquid	Distillation bottoms
			Solid	Distillation bottoms
Ethylene dichloride/ vinyl chloride	Direct chlorination	4,900	Aqueous	Acid scrubbers wastewater stripper
			Liquid and/or solid	Distillation residues
Ethylene glycol	Ethylene oxide hydration	1,960	Aqueous	Cooling tower purge, vent condenser condensate
			Liquid	Distillation residue
Ethylene oxide	Ethylene oxidation (air)	1,460	Liquid	Distillation bottoms
			Solid	Spent catalyst
	Ethylene oxidation (oxygen)	729	Liquid	Distillation bottoms
			Solid	Spent catalyst
Formaldehyde	Metallic silver catalyst	2,250	Aqueous	Ion exchange regeneration, cooling tower purge
	Metal oxide catalyst	750	Aqueous	Ion exchange regeneration, cooling tower purge

Table II-2. (Continued)

Product	Primary Process	Estimated 1978 Production (Gg/yr)[a]	Type of Waste	Waste Source
Glycol ethers	Reaction of alcohols with ethylene and/or propylene oxide	281	Aqueous	Vacuum system condensate
			Liquid	Distillation bottoms
Maleic anhydride	Benzene oxidation	135	Aqueous	Distillation, phase separation
			Liquid	Distillation residues
			Solid	Spent catalyst
Methanol	Low pressure	3,350	Aqueous	Distillation bottoms
			Liquid	Distillation side cut
Methyl methacrylate	Acetone cyanohydrin	398	Aqueous	Salt solution from neutralization, distillation
			Liquid	Spent sulfuric acid
			Solid	Polymeric residues formed in MMA reaction
Nitrobenzene	Benzene nitration	434	Aqueous	Sulfuric acid from stripper, nitrobenzene scrubber, caustic from neutralizer
Perchloroethylene/ trichloroethylene	Chlorination and oxychlorination of ethylene dichloride	300	Aqueous	Stripper bottoms
			Liquid and/or solid	Distillation residues

Table II-2. (Continued)

Product	Primary Process	Estimated 1978 Production (Gg/yr)[a]	Type of Waste	Waste Source
Propylene oxide	Chlorohydronation	500	Aqueous	Reaction/distillation
	i-Butane peroxidation[b]	280	Aqueous	Water wash, scrubbing, phase separation
			Liquid	Distillation residues
	Ethyl benzene peroxidation	130	Aqueous	Water wash, scrubbing, phase separation
			Liquid	Distillation residues
			Solid	Spent catalyst
Terephthalic acid (crude)	Air oxidation	1,985	Aqueous	Distillation
			Liquid	Distillation residues
1,1,1-Trichloroethane	Vinyl chloride	310	Aqueous	Scrubbing, phase separation
			Liquid/solid	Distillation residues
	Ethane	18	Aqueous	Scrubbing,phase separation
			Liquid/solid	Distillation residues

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[a] See ref 2.

[b] T-Butanol produced as co-product.

Frequently, two or more of the operations listed are involved in the generation of a single waste (e.g., the waste may be formed in one operation and separated in another operation). For this reason the waste sources shown tend to overlap to some extent. Following is a discussion of waste sources and the corresponding types of wastes which are common for each source category.

2. Distillation

a. Introduction——Distillation is widely used in the SOCMI for the separation of two or more components present in a liquid mixture. Separation is attained by partial vaporization, with the more volatile components tending to concentrate in the vaporized fraction. With conventional distillation the completeness of the separation is determined primarily by the relative volatility of the components, by the distillation column height, and by the reflux ratio used. Distillation is frequently used for the separation of wastes from process streams. The waste components may occur as either the more volatile (overhead) or the less volatile (bottoms) fraction.

b. Aqueous Wastes——Conventional distillation is widely used to separate water (introduced or formed in previous process steps) from single-phase organic-water solutions. Because separation by distillation is rarely totally complete, the water fraction will almost always contain some of the organic compounds present in the original solution, with the concentration determined primarily by the relative volatilities of water and the organic components. As shown by Table II-1 when water is the more volatile component and is removed overhead, the resulting aqueous waste will generally be relatively free of inorganic compounds or other solids contained in the original solution. However, if water is the less volatile component and is removed as the bottoms fraction, the aqueous waste will contain any inorganic compounds or other solids present.

Steam distillation is frequently used to purify organic compounds with relatively high boiling points that tend to decompose at the temperatures necessary for conventional distillation. The heat required for vaporization is supplied by the direct injection of steam, and the overhead stream is an organic-water vapor mixture. After condensation the overhead stream is separated into organic and aqueous phases (relatively low water solubility of the organics is necessary).

The aqueous layer, containing any soluble organics, is usually discharged as a waste source. From the standpoint of aqueous waste generation, steam distillation differs from conventional distillation in the following significant respects: (1) the concentration of organics in the aqueous waste is determined primarily by water solubility; with conventional distillation the organic concentration is primarily a function of the relative volatilities of water and the contained organics; (2) the source of water, which results in the formation of the aqueous waste, is primarily the steam distillation operation itself (i.e., the injected steam); with conventional distillation, water is introduced or formed in previous steps and is merely separated in the distillation operation.

Azeotropic distillation is frequently used when an organic-water separation by conventional distillation is not feasible because of unfavorable relative volatilities (often the result of the formation of an organic-water azeotrope). In this type of distillation a second organic compound, or drying agent, which forms a lower boiling azeotrope with water, is added, permitting overhead removal of a water-drying agent mixture. If the drying agent has low water solubility, it may be separated from the water by phase separation and recycled to the distillation operation and the water may be discharged as an aqueous waste source. If the drying agent has significant water solubility, an additional step will be required to separate water and the drying agent. If the aqueous waste is phase-separated, the organic concentration will depend primarily on the water solubility of the drying agent. When azeotropic drying is employed, the primary organic component in the aqueous waste is often the drying agent rather than the original organic compounds being dried.

c. Liquid Organic Wastes---Conventional distillation is frequently used to remove those liquid organics introduced as raw material contaminants or formed as unusable by-products in previous process steps. The liquid organic waste may occur as either the more volatile (overhead) fraction or the less volatile (bottoms) fraction. When the liquid organic waste is the more volatile component and is removed overhead, the resulting waste stream will generally be relatively free of inorganic compounds or other solids contained in the feed solution. However, if the waste is the less volatile component and is removed as the bottom fraction, it will retain any inorganic compounds or other solids.

Steam distillation is used primarily to separate organics with relatively high boiling points from less volatile compounds. The resulting liquid wastes, often in the form of high-boiling residues, are usually removed as the bottoms stream and may contain any inorganic compounds or other solids that were present in the feed solution.

When azeotropic distillation is used for water removal, significant quantities of liquid organic wastes are not usually generated.

d. Solid Wastes——In conventional distillation the solid wastes generated are almost always removed in the bottom fraction. They are usually removed as sludges or slurries or as liquids with high melting points that solidify when cooled to ambient temperature and will contain any inorganic compounds present in the feed solution.

In steam distillation the solid wastes generally have the same characteristics as those from conventional distillation.

Azeotropic drying does not usually generate solid wastes.

3. Water Contacting Operations

a. Introduction——Operations in which process streams are directly contacted with water are common throughout the SOCMI. This broad category includes a number of specific unit operations [e.g., absorption (scrubbing), quenching, extraction (water washing), and neutralization]. Although the purposes and the conditions of the specific operations vary significantly, the characteristics of the resulting wastes are generally similar. The general waste characteristics are given in Table II-1.

b. Aqueous Wastes——The predominant type of wastes resulting from water-contacting operations are aqueous wastes. Although the contact water is often recycled, a portion is usually discharged as an aqueous waste to remove impurities or by-products, which tend to accumulate in the recycled water. Additional water, initially present in the process stream, may be removed in the water-contact operation and will contribute to the quantity of aqueous waste (e.g., quenching of reactor effleunt which contains water vapor). The concentration of organics in aqueous wastes from water-contact operations is usually primarily dependent on the water solubility of the organics.

A primary function of water-contact operations is often the removal of inorganic compounds from process streams (e.g., acid gas absorption, extraction of salts, neutralization), which result in relatively high concentrations of inorganic compounds in the aqueous wastes.

c. Liquid Wastes——Although aqueous wastes are the predominant type of wastes from water-contact operations, organic liquid wastes with relatively low water solubility may be discharged with the aqueous waste and be subsequently separated (e.g., organic liquid wastes formed in gas-cracking operations may be discharged with effluent quench water).

d. Solid wastes——Similar to the manner in which liquid organic wastes may be generated by water-contact operations, semisolid residues (i.e., high-melting liquids, slurries, sludges) are frequently discharged with aqueous wastes from water-contact operations and subsequently separated. The resulting solid or semisolid waste usually contains a significant amount of water and may contain inorganic compounds present in the stream subjected to water contact.

4. Reaction

a. Introduction——Aqueous, liquid, and solid wastes are frequently formed in process reaction steps; however, the wastes formed are usually not discharged directly from the reaction vessel. The reactor effluent generally contains a mixture of wastes and usable process materials (i.e., raw materials, intermediates, products, usable by-products), and the wastes formed during reaction are usually actually discharged after a subsequent separation operation (e.g., distillation, phase separation, filtration).

b. Aqueous Wastes——Aqueous wastes may result from the formation of water as a reaction product, from the introduction of water to solutions or to mixtures of raw materials, or from the direct introduction of water into the reactor as a liquid or as steam. The concentration of organic and inorganic compounds in the resulting aqueous wastes will depend on subsequent separation operations, as well as on the composition of the feed to the reactor and the properties of the other reaction products.

c. Liquid Organic Wastes——Liquid organic wastes may be formed as normal reaction by-products or they may be introduced as raw material impurities or diluents. The intermittent generation of liquid organic wastes may also occur as a result of the temporary production of off-grade products that cannot be recycled or otherwise used in the process. The production of off-grade products most frequently occurs during startup or shutdown, during upsets caused by uncontrolled variations in process conditions, or from the unintentional use of off-grade raw materials or catalysts.

As with the aqueous wastes, the characteristics of liquid organic wastes (e.g., concentration of water or inorganic compounds) may be influenced by subsequent separation steps, as well as by the conditions governing the reaction and composition of the feed.

d. Solid Wastes——Solid wastes may be generated from normal reaction by-products, from raw-material impurities or diluents, or from the discharge of spent catalyst. As with liquid organic wastes, solid wastes may also be generated by the temporary production of off-grade products, which occurs during normal startups and shutdowns or during process upsets. The characteristics of solid wastes may also be influenced by subsequent separation steps.

5. Gas Compression and Vacuum Generation

a. Introduction——Gas compression and vacuum generation, common operations in processes within the SOCMI, are, in general, accomplished either with rotary mechanical devices (e.g., centrifugal and reciprocating compressors, vacuum pumps) or with venturi devices (e.g., steam- or water-jet ejectors). Significant quantities of wastes are generated in these operations. The general characteristics of wastes and generation mechanisms associated with the two types of devices (i.e., rotary or venturi) differ significantly and are discussed separately.

b. Rotary Devices——Aqueous wastes are frequently generated when organic gases containing water vapor are compressed and subsequently cooled to remove the heat of compression, condensing water vapor along with an equilibrium quantity of the compressed organic compounds. If the contained organic compounds have low water solubility, the condensed liquid is usually phase-separated to remove the insoluble organics before the aqueous waste is discharged. In this case the concentration of organics in the aqueous waste is primarily dependent on the degree of water solubility of the organics. If the contained organics have significant water solubility and cannot be readily separated, the concentration of organics in the aqueous waste will depend primarily on the relative volatilities of the water and the organic compounds. Aqueous wastes from this source may contain inorganic compounds present in the compressed vapor (e.g., acid vapors).

Water or aqueous solutions are frequently used as sealing fluids in rotary vacuum pumps, resulting in the generation of significant quantities of aqueous wastes. Vacuum pumps of this type cause intimate contact between the vapor removed and the sealing fluid and sometimes serve the dual functions of vacuum generation and vapor scrubbing (e.g., acid vapors can be removed, using caustic solution as the sealing fluid). The resulting aqueous wastes can contain significant concentrations of inorganic compounds, as well as equilibrium concentrations of any organics present in the vapor removed.

Liquid organic wastes are frequently condensed and separated during the compression of organic vapors in the same manner as the aqueous wastes discussed in the previous section. The injection of compressor lubricating oil, required for sealing or for piston and packing lubrication, may also contribute to the generation of liquid waste. Liquid wastes that occur with the use of rotary vacuum pumps are generated primarily from the discharge or loss of sealing fluid. If the sealing fluid is an aqueous solution, the contained insoluble liquid organic wastes are frequently phase-separated before they are discharged. If organics are used as a sealant (e.g., oil), the discharge of spent sealant or the entrainment of sealant and subsequent separation from the discharged vapor can result in the generation of liquid waste.

Solid wastes in significant quantities are not usually generated in compression and vacuum generation operations. Minor quantities of polymers or other solid residues may be formed during compression and may have to be removed from the equipment periodically.

c. Venturi Devices——Aqueous wastes are generated when venturi devices, such as steam- and water-jet ejectors, are used for vacuum generation. These devices develop vacuum by directly contacting the vapor removed from the evacuated vessel with a high-velocity jet of steam or water in a venturi throat. The effluent water (steam is usually subsequently condensed) will contain the soluble organic or inorganic components that were originally present in the vapor contacted, resulting in the generation of aqueous wastes. The concentration of organics in the discharged aqueous waste is generally relatively low. Since jet ejectors cause intimate contact between the effluent vapor and the motivating fluid (steam or water), they frequently serve the dual functions of vacuum generation and vapor scrubbing. When the gases that are removed contain significant concentrations of acid vapors, caustic solution instead of water may be circulated through the venturi, which will result in relatively high concentrations of inorganic salts in the aqueous wastes.

Liquid organic wastes may occur when venturi devices are used for vacuum generation. Organics contained in the removed gas may be condensed and removed with the effluent aqueous waste. If the condensed organics have low water solubility, they may subsequently be phase-separated from the aqueous waste stream and discharged as a separate waste stream composed primarily of liquid organic compounds.

Solid wastes containing significant quantities of organic compounds are not usually generated by venturi-type devices.

6. Solid-Liquid Separation

a. Introduction——The separation of liquids from solids, accomplished primarily by flotation, sedimentation, and filtration, can result in the generation of primarily aqueous and solid wastes. Liquid-solid separations are frequently used to separate wastes that are formed as normal-process by-products, introduced with raw materials as contaminants or diluents or introduced as catalysts or other process aids that must subsequently be removed.

b. Aqueous Wastes——Aqueous wastes are frequently generated when solid products or intermediates, precipitated in aqueous solutions, are subsequently filtered. The discarded filtrate may contain significant quantities of organic compounds. The filtrate generally contains an equilibrium concentration of the product, whose concentration is determined by the solubility of the product in the filtrate solution. Other organic components in the filtrate may include unreacted organic raw materials and soluble organic by-products.

The concentration of inorganic compounds in discarded filtrate solutions is often significant. Inorganic compounds are frequently added in excess as raw materials, and salts are frequently formed as normal-reaction by-products. Inorganic salts may also be added to reduce product solubility, thereby reducing product losses in the filtrate.

Products or intermediates that have been precipitated from aqueous or organic solutions and subsequently separated are frequently washed with water to remove residual organic or inorganic raw materials or by-products. The effluent wash water, usually discharged as an aqueous waste, will contain most of the components contained in the initial filtrate although usually in much lower concentrations. The concentration of the separated product in the discharged wash water, however, will be dependent on water solubility and may be greater than in the initial filtrate if the other components, present in much higher concentration in the initial filtrate, reduce product solubility.

c. Liquid Organic Wastes——Significant quantities of liquid organic wastes are not usually generated from liquid-solid separation operations. When precipitation occurs in an organic solution or when the filtered precipitate is washed with an organic solvent instead of water, the solvent is usually recovered by distillation and then recycled.

d. Solid Wastes——Solid wastes generated from liquid-solid separation operations are of two general types: solids of primarily inorganic composition containing relatively small quantities of liquid or solid organic compounds and solids of primarily organic composition usually in the form of slurries or sludges, which frequently contain significant quantities of water and inorganic salts.

Solid wastes that are primarily of inorganic composition may be generated from normal reaction by-products, from raw material impurities, from the discharge of spent catalyst (i.e., the solid spent catalyst is discharged from the reactor with liquid reaction products and is subsequently removed by liquid-solid separation), and from the discharge of inorganic compounds used for filter precoating (e.g., diatomaceous earth).

Solid wastes composed primarily of organic compounds frequently result from the formation of heavy residues or polymers as undesirable by-products in process equipment and storage tanks. These wastes are frequently transported as liquid-solid mixtures (e.g., slurries, flocs, suspensions) and are subsequently separated.

A major source of solid wastes that fall within this category is activated sludge, which is formed in biological waste treatment systems. Activated sludge is usually separated from the effluent wastewater by sedimentation (settling), followed by various dewatering techniques.

7. Adsorption

a. Introduction——Adsorption is frequently used in the SOCMI for the separation of gaseous or liquid components present in relatively low concentrations from the respective gaseous or liquid streams. At high concentrations other separation techniques (e.g., distillation) are usually more suitable. The most common adsorbent and the one generally used for the removal of organic compounds from air (oxygen and/or nitrogen) and from water is activated carbon. Other adsorbents, such as activated alumina, molecular sieves, and silica gel, are less common and are most frequently used for the removal of water and other polar compounds from organic gas or liquid streams. Aqueous, liquid, or solid wastes may be generated by adsorption processes.

b. Aqueous Wastes——When aqueous streams are treated by adsorption to remove contained organic compounds, the separation is rarely totally complete. The concentration of organics in the effluent water (usually discharged as an aqueous waste) will depend on a number of factors, including the inlet concentration, the affinity of the adsorption media for the specific organic compounds, and the mass flow rate through the bed. The effluent concentration will usually increase slowly as loading of the bed is continued, until the concentration of organics in the bed reaches the "breakthrough" point. If loading is continued beyond breakthrough, the effluent concentration of organics will increase rapidly and will eventually reach the inlet concentration if not terminated. The concentration of inorganics present in the treated aqueous stream is usually not significantly changed as it passes through the adsorbent bed.

Aqueous wastes may also be generated during the regeneration (i.e., removal of adsorbed organics) of adsorbents treating either gaseous or liquid streams when in-place, nondestructive regeneration techniques are used. In-place regeneration is more commonly used for treatment of gases than for treatment of liquids. The most common method for in-place, nondestructive regeneration consists of passing steam through the bed, with the adsorbed organics being eluted with the effluent steam. After condensation of the effluent the organics may be phase-separated and the aqueous phase discharged directly as an aqueous waste if the organics have low water solubility. If the organics have significant solubility and their value justifies recovery, an additional recovery step will be required (e.g., distillation). Other regeneration techniques (e.g., pH change, solvent regeneration), which are less common, may result in the generation of aqueous wastes.

When adsorbents (e.g., alumina, molecular sieves) are used for the removal of water from organic streams, the adsorbent bed is usually periodically regenerated to remove the adsorbed water. This is usually accomplished by passing heated gas (e.g., methane, nitrogen) through the bed. On cooling of the effluent gas most of the contained water is condensed and is usually discharged as an aqueous waste.

c. Liquid Wastes——Liquid organic wastes resulting from the treatment of gas or liquid streams by adsorption generally occur when the adsorbed organics are of little or no value or when the cost of purification is excessive. The organics recovered during regeneration may then be discharged as a liquid waste.

d. Solid Wastes——Solid wastes, which may contain significant quantities of organic compounds, generally occur when spent adsorbents (e.g., activated carbon, alumina) are discarded. In most applications adsorbents tend to lose activity, or adsorption capacity, with extended use as the result of a gradual loss of effective surface area.

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When activated carbon loses activity, it is usually removed from the adsorber and thermally treated in a furnace, where the carbon is partly oxidized. When carbon usage is small, regeneration may not be practical and spent carbon may be discarded as a solid waste.

8. Storage

a. Introduction——The formation and/or separation of water and residues in storage tanks for organic liquids frequently results in the generation of wastes, primarily in the form of either aqueous wastes or semisolid sludges.

b. Aqeuous Wastes——Water frequently accumulates as an insoluble layer in organic liquid storage tanks and is periodically drained off and discharged as an aqueous waste. The water phase may be introduced with the stored organic liquids as an emulsion that separates on standing, or it may result from the leakage of rainwater into open-top or floating-roof tanks. The concentration of organics in the discharged aqueous waste is usually determined by the water solubility of the organics. The discharged aqueous waste may contain inorganic compounds when they are present in the incoming water.

c. Solid Wastes——Solid residues (e.g., polymers) are occasionally formed in organic liquid storage tanks, usually due to the slow degradation or polymerization of contained liquid organics. If the residues are more dense than the liquid, they will tend to collect in the bottom of the tank and may be periodically drained off as a sludge or slurry. If the particles tend to remain in suspension, the discharged organic liquid may have to be filtered or centrifuged. The collected solids are then usually discharged as solid wastes.

9. General Process Area

a. Introduction——Aqueous, liquid, and solid wastes frequently result from a number of miscellaneous conditions or occurrences that are common in the SOCMI. Included are relatively small but frequent or continuous leaks from equipment, piping, and storage tanks; accidental spills resulting from equipment failure or operating errors; the normal generation of waste or discharge of materials occurring during maintenance activities (i.e., shutdowns, equipment repair, equipment cleanout);

washdown of process areas; and rainfall runoff. As the actual generation of wastes will frequently result from combinations of these conditions or events, there is some overlap in the waste sources discussed.

b. Aqueous Wastes——Aqueous wastes frequently result from the flushing of equipment for cleanout purposes or in the preparation of equipment for maintenance, process area washdown, and storm runoff. The organics in aqueous wastes from area washdown and storm runoff generally result from equipment leaks and/or spills.

c. Liquid Wastes——Liquid organic wastes can result from equipment leaks, spills, and drainage of equipment before or during maintenance operations. Frequent sources of organic liquid leaks are pump mechanical seals and packing glands.

d. Solid Wastes——Solid wastes can result from spills of solid materials and from solid residues removed from equipment and piping during cleanout and maintenance operations.

C. REFERENCES*

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2. Chemical Economics Handbook Manual of Current Indicators, Supplemental Data, Stanford Research Institute, Menlo Park, CA.

*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

III. SECONDARY EMISSION SOURCES

A. INTRODUCTION

Secondary emissions result from the handling, treatment, and disposal of the wastes described in Sect. II. Table III-1 provides an overview of the waste treatment or disposal methods that are generally applicable to the waste categories shown in Table II-1. The resulting secondary emissions are determined by both the characteristics of the wastes and the treatment or disposal methods used. The following discussion covers the most significant treatment and disposal methods and the general waste categories for which these methods are applicable. As was the case for the waste sources, the generic classifications of treatment and disposal methods tend to overlap to some extent (e.g., physical separation steps are integral parts of a biological treatment system). Mention is made of operations and processes described as waste sources in Sect. II that are also included as waste treatment or disposal methods or secondary emission sources in this section. The distinction between the waste sources and the secondary emissions sources is determined by the function of the operation. If its primary function is the treatment or disposal of aqueous, liquid, or solid waste, then it is considered to be a secondary emission source. The distinction is not always clear. An operation may be both a waste source and a secondary emission source [e.g., a biological treatment system treats aqueous wastes (waste treatment system) and discharges aqueous waste and solid waste or sludge (waste source)].

B. PHYSICAL SEPARATION METHODS

1. Introduction

Physical separation methods do not actually destroy or dispose of aqueous, liquid, and solid wastes but remove or reduce the concentration of components, thereby rendering the wastes more acceptable or amenable to subsequent disposal methods. For this reason essentially all physical separation operations for treating wastes are also waste sources and the actual disposal of the wastes may result in additional secondary emissions.

Table III-1. Summary of Waste Characteristics and Corresponding Common Treatment Operations

Treatment/Disposal Operations	Aqueous							Liquid Organic				Solids, Slurries, and Sludges			
	Organic Conc.														
	Trace—1,000 ppm	1,000—10,000 ppm	>10,000 ppm	Contains Dissolved Inorganics	Contains Suspended Solids	Basic-pH, >10	Acidic-pH, <4	Contains Organics Only	Contains Dissolved Inorganics	Contains Suspended Solids	Contains Water	Organics Only	Contains Inorganics	Contains Heavy Metals	Contains Water
Physical Separation Methods															
Conventional distillation								X	X	X	X				
Steam stripping	X	X	X	X	X										
Phase separation/emulsion breaking		X	X	X	X			X	X	X	X				
Adsorption	X	X		X											
Extraction		X	X	X		X	X								
Liquid/solid separation	X	X		X	X							X	X		X
Chemical Treatment															
Neutralization	X	X		X		X	X								
Precipitation/coagulation				X	X	X	X								
Chemical oxidation	X	X		X											
Thermal Destruction			X					X	X	X	X	X	X	X	X
Biological Treatment	X	X	X												
Terminal Storage															
Landfill								X	X	X	X	X	X	X	X
Surface impoundment	X	X	X	X	X	X	X	X	X	X	X				
Deep-well				X	X	X	X	X	X	X	X				
Dilution in Neutral Water	X														

2. Steam Stripping

a. Aqueous Wastes——Steam stripping is most frequently used to reduce the concentration of organic components present in aqueous wastes. Steam stripping is similar to steam distillation (Sect. II-B-2-b) in that volatilization is attained by the direct sparging of steam into the liquid phase. The distinction between steam stripping and steam distillation lies in the components that are separated. Steam stripping is used to remove organics from aqueous solutions. Steam distillation is used primarily to separate relatively high boiling organics from higher boiling impurities or residues.

As with steam distillation, the overhead vapor from a steam stripper is a mixture of steam and the organic components removed from the original solution. If the contained organic compounds have low water solubility, the condensed overhead stream separates into aqueous and organic phases. The organic phase may be further processed to reduce the water content (e.g., conventional distillation) and be returned to the process or discharged as an organic liquid waste. The aqueous phase, which often has approximately the same organic concentration as the stripper feed has, may be recycled to the stripper. The bottoms stream from the stripper is discharged as an aqueous waste stream.

Secondary emissions from steam stripping result primarily from the venting of gases contained in the overhead stream, which are not condensed (primarily air). The quantity of contained VOC that is vented is generally determined by the quantity of noncondensable gases vented, the vapor pressure(s) of the organic component(s), and the effective condenser temperature.

b. Liquid Organic Wastes——Steam stripping is not generally used for the treatment of liquid organic wastes.

c. Solid Wastes——Steam stripping may be used for the treatment of solid wastes that either are primarily inorganic but contain significant quantities of volatile organic compounds (e.g., spent catalyst, spent adsorbents, filter aids, precipitates) or are primarily composed of organic solids with low volatility but contain significant quantities of organic compounds of relatively high volatility (e.g., activated sludge). The main purpose for steam stripping is to reduce emissions of VOC from the solids during subsequent handling and disposal operations. As with the steam stripping of aqueous wastes, emissions of VOC occur mostly with the venting of noncondensable gases.

3. Conventional Distillation

a. Aqueous Wastes——Conventional distillation is seldom used in the treatment of aqueous wastes unless the concentration and quantity of organic compounds that can be recovered are sufficient to justify the energy requirements. Steam stripping is generally more suitable for solutions with very low concentrations, possibly followed by the conventional distillation of the stripper overhead if the contained organics and water have significant mutual solubility. As with steam stripping, emissions mainly result from the venting of noncondensable gases and are usually relatively low.

b. Organic Liquid Wastes——The conventional distillation of liquid organic wastes may occur as a pretreatment step to render the wastes more amenable to final disposal methods (e.g., removal of water or inorganics prior to combustion or removal of highly volatile, noxious, or hazardous components prior to disposal). Emissions result mainly from the venting of noncondensable gases.

4. Liquid-Liquid Phase Separation/Emulsion Breaking

a. Aqueous Wastes——Phase separation and/or emulsion breaking operations are frequently used to separate aqueous wastes from organic liquids that have relatively low water solubility. The most common methods of phase separation and/or emulsion breaking include density differential separation (e.g., API oil/water separators, plate separators, centrifuges), filtration/coalescence separation (e.g., granular media, fibrous media), and chemical separation (e.g., acid-alum-lime process, polyelectrolyte addition). The most significant emissions occur from the vaporization of organic compounds when separation vessels or basins such as API separators and plate separators are open-topped, a relatively common practice throughout the SOCMI. Emissions from enclosed or covered vessels are generally much less than those from open-top vessels although they may be significant if vented without additional controls.

b. Liquid Organic Wastes——Phase separation of aqueous wastes and liquid organic wastes frequently precedes final treatment or disposal operations when separate disposal methods are used for the aqueous wastes and the liquid organic wastes (e.g., aqueous wastes are biologically treated and liquid organic wastes are incinerated). The comments concerning emissions from the previous section also apply to liquid organic wastes.

c. Solid wastes——Liquid-liquid phase separation is not applicable to solid wastes.

5. Solid-Liquid Separation

a. Introduction——Solid-liquid separation operations, including sedimentation (clarification, thickening), flotation, filtration, and centrifugation, are frequently used in the SOCMI for the treatment of aqueous, liquid, and solid wastes. These specific unit operations frequently occur as integral steps within more inclusive treatment processes [e.g., following biological treatment, aqueous waste is separated from activated sludge by clarification and thickening (sedimentation)]. The thickened sludge may be further dried (dewatered), and the residual suspended solids in the aqueous waste effluent may be further reduced by filtration.

b. Aqueous Wastes——The most significant emissions occur from the vaporization of volatile organic components when separation vessels, such as settling basins, clarifiers, and thickeners, are open-topped, a relatively common practice in the SOCMI. Emissions from enclosed or covered vessels are generally much less than those from open-topped vessels although they may be significant if vented without additional controls.

c. Liquid Organic Wastes——Liquid-solid separation operations used in the treatment of wastes are less common for liquid organic wastes than for aqueous wastes. Liquid organic wastes containing solids may require separation as a pretreatment step prior to final disposal (e.g., solids are removed by filtration before incineration of liquid organic wastes to prevent clogging of incinerator atomizing nozzles); however, emissions from this type of source are relatively minor.

Frequently operations whose function is either liquid/solid separations (e.g., settling basins) or liquid/liquid phase separations (e.g., API separators) may provide a three-way separation (i.e., aqueous liquid, insoluble organic liquids,

and solids), with the liquid/liquid phase separation taking place in the upper part of the vessel and the settled solids being removed from the bottom. The emissions of volatile organic compounds from open-topped vessels may be significantly greater when insoluble liquid organics separate as an upper layer.

d. Solid Wastes——Solid wastes are discussed above.

C. CHEMICAL TREATMENT

1. Introduction

The chemical treatment and disposal processes described in this section include both those used for the terminal treatment of SOCMI wastes and those used as pretreatment steps to render the wastes more amenable to terminal treatment. Major categories of chemical treatment methods discussed in the following sections include neutralization, precipitation, and chemical oxidation. As was true for liquid/liquid and solid/liquid separation operations, chemical treatment operations frequently take place in open-topped vessels or basins or in covered vessels that are vented without control. Emissions result chiefly from the vaporization of organic components contained in the wastes.

2. Neutralization

a. Aqueous Wastes——In many manufacturing operations within the SOCMI large quantities of acidic or alkaline aqueous wastes are discharged. Most regulatory codes specify that the pH of any effluent discharge should not be lower than 6 or higher than 9 units. Neutralization to a similar pH range is also generally required in biological treatment systems when acid or alkaline characteristics of the wastewaters would otherwise interfere with or retard biological activity. Neutralization is accomplished by the addition of alkali to acids or of acid to alkalis as required to effect the desired pH adjustment. Neutralization process equipment generally consists of open-topped or covered neutralization basins, mixing devices, and neutralizing agent feed, storage, and control facilities. Emissions generally result from the vaporization of contained organic compounds from the surface of the liquid in the neutralization basin.

b. Liquid Wastes——Neutralization as a waste treatment operation is not generally applicable to liquid organic wastes.

c. Solid Wastes——Neutralization as a waste treatment operation is not usually applicable to solid wastes; however, solid wastes, often composed of relatively insoluble inorganic salts, may be formed as precipitates during neutralization and may require a subsequent solid/liquid separation step.

3. Precipitation and Coagulation

a. Aqueous Wastes——Chemical precipitation is a process in which chemicals are added to react with specific constituents to form insoluble products that can be removed in a subsequent solid-liquid separation step, such as by sedimentation or filtration. In wastewater treatment, precipitation processes are perhaps most commonly associated with the removal of such heavy metals as zinc, nickel, cadmium, and lead. Metals are generally precipitated as the hydroxide or carbonate species. If the precipitate is formed as a colloidal dispersion that cannot be removed by a conventional sedimentation or filtration process, a coagulation step may be added. Coagulation may be defined as the addition of chemicals to cause aggregation of the dispersed colloidal particles and to permit separation by conventional sedimentation or filtration. Precipitation/coagulation operations and the ensuing sedimentation or filtration operations frequently take place in open-topped basins or tanks. Emissions result chiefly from the vaporization of contained organics.

b. Organic Liquids——Precipitation/coagulation as a waste treatment operation is not generally applicable to liquid organic wastes unless the wastes also contain a significant concentration of water.

c. Solid Wastes——Precipitation is not applicable to solid wastes. Coagulation may be used to aid in the removal of finely dispersed particles of solids contained in aqueous wastes.

4. Chemical Oxidation

a. Aqueous Wastes——Chemical oxidation is used to chemically modify waste streams either by completely oxidizing the organics to CO_2 and H_2O or by partially oxidizing the organics to detoxify them. These waste streams are usually aqueous wastes that cannot be handled directly by biological oxidation (either because of organic strength or bioinhibitory characteristics) or incineration (because the organic concentration is too low or there is excessive corrosion caused by the presence of inorganic salts or halogens). Oxidation is also used to purify aqueous streams (such as waste sodium chloride brines) to permit recycling. Most of the chemical oxidation processes are based on one of two oxidizing agents——chlorine or oxygen. Because chemical oxidation processes currently have relatively limited use and enclosed vessels are generally required (to conserve oxidizing agents or because elevated temperatures and pressure are required), secondary emissions of VOC from these processes are generally relatively low compared with emissions from the more conventional aqueous waste treatment methods.

b. Liquid Organic Wastes——Chemical oxidation is not generally applicable.

c. Solid Wastes——Chemical oxidation is not generally applicable.

D. THERMAL DESTRUCTION

1. Introduction

Thermal destruction or incineration is widely used within the SOCMI for the disposal of liquid and solid organic wastes. Because of high supplemental energy requirements to vaporize and heat the contained water, thermal oxidation is not generally used for the disposal of large quantities of aqueous wastes unless the more conventional treatment methods (usually biological) are not suitable.

Emissions of VOC from thermal destruction processes result primarily from the incomplete combustion of hydrocarbons, with residual organic compounds being discharged in the flue gas. The destruction efficiency, or VOC removal efficiency, is dependent on a number of factors, including the combustion zone temperature, the residence time at the combustion temperature, the degree of turbulence in the combustion zone, the percentage of excess air or oxygen (above stoichiometric requirements), the composition and physical characteristics of the wastes, and the specific design features of the incinerator.

In general, incinerator design and operating requirements for the effective destruction of liquid wastes are less demanding than those than for the destruction of solids. The chemical composition of the contained organic compounds in both liquid and solid wastes is very significant. The difficulty of attaining high VOC removal efficiency generally increases with increasing molecular weight and with the increasing carbon:hydrogen ratio of the organic compounds.

The presence or concentration of the following waste components may determine the suitability of thermal destruction as a disposal method or influence the incinerator design and flue-gas treatment requirements:

Water, if present in an excessive amount, may result in the heat of combustion of the contained organics being insufficient to attain the required temperature and auxiliary fuel will be required.

Sulfur will result in the presence of SO_2 in the flue gas and may require flue gas treatment.

Halogens (primarily Cl^-) will result in the presence of HCl (HBr, Br_2, Cl_2) in the flue gas, which may cause severe corrosion problems and may require flue-gas treatment.

Salts may cause excessive salt particulates in the flue gas, which are difficult to remove by flue-gas treatment, and may form low-melting slag, possibly causing operating problems with conventional incinerators.

Phosphorous may form particulates that are difficult to remove by flue-gas treatment.

Combined nitrogen may form excessive NO_x in the flue gas, which is difficult to remove by flue-gas treatment.

The concentrations of highly toxic compounds, e.g., mercury, arsenic, and cyanides, in vented flue gas must be extremely low; they are difficult to reduce to acceptable levels by flue-gas treatment. Heavy metals may be leached from ash to form highly toxic aqueous wastes.

Many types of incinerators are manufactured, and each type is basically designed for specific waste profiles. Most systems will handle liquids to some degree but significant variations exist in sludge and solids handling capabilities. The most prevalent types of incinerators are single-closed-chamber, rotary-kiln, multiple-hearth, and fluid-bed units. In addition, liquid wastes with favorable flue-gas characteristics (i.e., low toxicity, noncorrosive, low particulate concentration) are frequently burned as supplementary fuel in direct-fired boilers and process furnaces.

Other thermal destruction processes that currently have rather limited industrial application include catalytic oxidation and pyrolysis processes.

2. Aqueous Wastes

Because of their high energy requirements, large quantities of aqueous wastes containing relatively low concentrations of organic compounds are not generally treated by thermal destruction methods; however, if the wastes are not amenable to biological treatment (usually due to toxicity or poor biodegradability), thermal destruction may be the most suitable alternative. When possible, aqueous wastes are usually burned with organic liquid wastes to minimize or eliminate the need for auxiliary fuel (i.e., oil, gas). Other than the supplementary fuel requirements, incineration requirements and VOC emissions resulting from the combustion of aqueous wastes are generally similar to those for liquid wastes, discussed in the next section. Aqueous wastes frequently contain significant quantities of soluble inorganic compounds, which may result in the problems and/or corresponding incinerator requirements discussed in Sect. III-D-1.

3. Liquid Wastes——Most of the types of incinerators discussed in Sect. III-D-1 can handle liquid wastes; however, if concurrent thermal destruction of solid wastes is not required, a relatively inexpensive closed-chamber incinerator or a boiler or process furnace combustion chamber can generally be used. The thermal destruction of liquid wastes in boilers or process furnaces is generally limited to wastes that do not form flue gas that is severely corrosive or requires extensive treatment before discharge.

The characteristics of the emissions resulting from the thermal destructon of liquid wastes are dependent on the waste characteristics and incinerator parameters discussed in Sect. III-D-1.

4. Solid Wastes

Of the types of incinerators discussed in Sect. III-D-1, the rotary-kiln, multiple-hearth, and fluid-bed incinerators are all designed for the thermal destruction of solid wastes, although all of them can concurrently handle liquid wastes. Features incorporated in solid-waste incinerators, which are generally not necessary for the combustion of liquids, include a feed mechanism, an ash removal system, and a means of tumbling or agitating the wastes to achieve complete burnout. Rotary-kiln incinerators also usually require a secondary combustion chamber (complete combustion of vapors released when the solid wastes are heated cannot generally be attained in the primary chamber).

The characteristics of emissions resulting from the thermal destruction of solid wastes are dependent on the waste characteristics and incineration parameters discussed in Sect. III-D-1.

E. BIOLOGICAL TREATMENT

1. Introduction

Biological waste treatment is a generic term applied to a variety of processes that utilize active microorganisms to convert primarily organic constituents in aqueous wastes to more stable forms. Biological waste treatment processes essentially simulate the biological reactions that would occur in the environment. However, since biological processes generally employ high concentrations of active microorganisms under controlled conditions, the decomposition rates of degradable materials are vastly accelerated.

In general, biological processes are applicable to the treatment of soluble, degradable organics in the concentration range of 0.01 to 1%. Removal efficiencies can vary from 50 to 99+% (BOD or COD), depending on the process configuration, the loading factor, and the nature and distribution of organic material present in the wastewater.

The major process equipment in biological treatment is basically a reactor to provide contact between the wastewater and the microorganisms and to introduce air or oxygen (aerobic processes only), a solids-liquid separation device (such as a settling tank or clarifier), sludge recycle pumps, and monitoring and control devices. Equipment for pH control and/or nutrient addition may also be required. Highly concentrated or variable waste loads may necessitate the use of an equalization basin before treatment. Finally, solids handling devices for final sludge treatment and disposal may be necessary. A simplified flow diagram for a conventional activated sludge treatment plant is shown in Fig. III-1.

Biological waste treatment operations (i.e., aeration, biomass-wastewater contact, solid-liquid separation) usually take place in open-topped basins or vessels. (Some of the newer and less widely used processes such as fluid-bed and enriched oxygen processes utilize enclosed vessels.) Most of the VOC emissions result from the vaporization of organic compounds in the aqueous wastes as they pass through the various process steps. The quantity of VOC emissions is for the most part a function of the organic concentration in the aqueous waste, of the solubilities of the organic components, and of their vapor pressures. (The factors affecting emissions are discused in more detail in Sect. IV.)

2. Aqueous Wastes

Biological waste treatment is used almost exclusively for the treatment of aqueous wastes (0.01 to 1.0% concentration). The amenability of specific aqueous wastes to biological treatment is dependent on the composition and concentration of both the organic and the inorganic components present.

Many chemical compounds that are biodegradable in dilute solutions may inhibit biological activity when they appear in a concentrated form. Other components, such as metallic or cyanide ions, are toxic to biological organisms at certain concentration levels. The actual concentration at which biological activity is inhibited is difficult to determine for each separate compound.

Biological processes generally operate effectively only within a relatively narrow pH range (approximately 6 to 9). The biological treatment of alkaline or acidic wastes usually requires preneutralization to within this pH range by the addition of either acid or alkali (see Sect. III-C-2). An open-topped basin is also usually used for neutralization, and therefore additional emissions of VOC may occur.

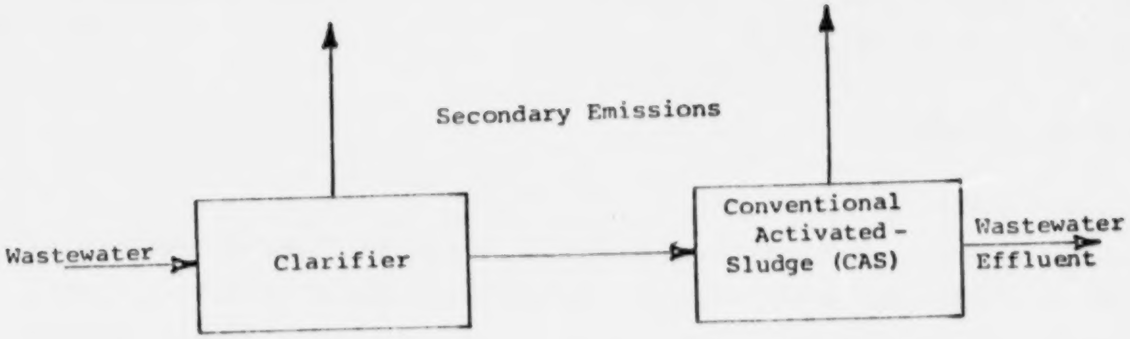

Fig. III-1. Conventional Activated Sludge Treatment Plant

3. Liquid Organic Wastes

Biological treatment processes are not generally used for the treatment of concentrated liquid organic wastes.

4. Solid Wastes

Biological treatment is not generally used for the treatment of solid wastes; however biological processes are almost always sources of solid wastes, which are in the form of sludges. The disposal of activated sludge discharged from biological treatment processes may result in additional secondary emissions of VOC. (Terminal disposal of activated sludge is usually either by storage in landfill or by incineration.)

F. TERMINAL STORAGE

1. Introduction

Terminal storage, which includes landfilling, impoundment, and deep-well injection, is widely used in the SOCMI for the ultimate disposal of aqueous, liquid, and solid wastes. The significant number of incidents involving the contamination of natural waters (groundwater and surface water) by toxic chemicals, which were caused by poor waste storage practices, has brought terminal storage as a means of waste disposal under criticism. Although the prevailing environmental objectives are aimed at minimizing the use of terminal storage for the disposal of hazardous or toxic wastes, there are currently no feasible alternatives for certain wastes. However, if approved storage practices are observed, wastes can be stored with minimal adverse effects on the environment.

Emissions of VOC from the landfilling and impoundment of wastes containing organic compounds may be significant, depending on the concentration and properties of the compounds in the wastes and on the storage procedures used. Well-designed deep-well disposal systems for liquid wastes generally result in minimal secondary emissions.

2. Landfill

a. General——A landfill, as opposed to an open dump, is the engineered burying of wastes in which consideration is given to the geological, hydrogeological, and climatic conditions at the site, to the type, quantity, and physical properties of the materials being dumped, and to the ultimate redevelopment of the land after the landfill site has been closed. The most important single consideration in selection of the landfill site is protection of the quality of associated natural waters.

A naturally secure landfill is one situated on bedrock, shale, or other impervious materials that prevent the seepage of leachate into groundwater, or the site may be one where there is no groundwater nearby. When naturally secure sites do not exist, liners made of natural or synthetic materials are used.

The important secondary-emission parameters are the physical and chemical properties of the wastes, the water content of the landfill soil, the physical and chemical properties of the soils, the rate of air flow across the surface of the landfill, and the biodegradability of the organic waste components. Secondary emissions from landfilling are discussed more fully in Sect. IV-F.

Landfarming,[1] which may be defined as the use of the upper soil layer (upper 6 to 8 in.) for the biological treatment/disposal of wastes, is receiving considerable attention although it is not currently widely used. Landfarming is primarily suitable for the disposal of nonhazardous liquid and solid wastes with relatively low vapor pressures. Although no specific data on secondary emissions from landfarming are available, the similarity of landfarming to landfilling would indicate comparable secondary emissions and the following discussion of secondary emissions from landfilling also generally applies to landfarming.

b. Aqueous Wastes——Landfilling is generally not suitable and is seldom used for the disposal of large quantities of aqueous wastes. When not amenable to biological treatment (due to poor biodegradability of organics or to significant concentrations of toxic inorganic components), when impoundment is not an acceptable alternative, or when deep-well disposal facilities are not available, landfilling may be used for the disposal of relatively small quantities of aqueous wastes. The comments regarding landfilling practices and the corresponding secondary emissions for liquid organic wastes generally also apply to the landfilling of aqueous wastes.

c. Liquid Wastes——Bulk liquids normally require special approval to be landfilled. One method of minimizing the potential for migration of liquids is to keep the liquid content below the absorptive capacity of the solid materials (solid wastes and back-filled soil) in the landfill. When this is done, the secondary emissions resulting from the landfilling of liquid wastes are essentially the same as for solid wastes or sludges.

Stabilization or encapsulation of free liquids is required at many landfill sites before liquid wastes are accepted for storage. Although various chemical fixation and encapsulation methods have existed for some time, current concerns with hazardous materials in landfills and new regulations have resulted in extensive research being undertaken in these areas. Although the main purpose of stabilization is usually to prevent the leaching of water-soluble components, it is also often effective in controlling secondary emissions. Stabilization is further discussed in Sect. V-E-5.

Drums and other containers are also used when liquids are landfilled, but problems can occur in the landfill when the containers deteriorate, causing leakage of stored liquids; therefore drums of liquids are limited to the absorptive capacity of the filled solids in most landfills, as are bulk liquids.

d. Solid Wastes——The greatest quantity of wastes disposed of by landfill are solid wastes and sludges. Generally, terminal disposal options for solid organic wastes are limited to either landfilling or incineration, and for solid wastes composed principally of inorganic compounds landfilling is usually the only feasible option, with the possible exception of ocean dumping.

Secondary emissions resulting from the landfilling of solid wastes and sludges depend primarily on the concentration and vapor pressure of the organic material and on the rate of diffusion through the air surrounding the chemically covered surface. Secondary emissions resulting from landfilling solid wastes are discussed in more detail in Sect. IV-F.

3. Surface Impoundment

a. Introduction——Surface impoundment in open ponds or basins is frequently used for the storage of aqueous and liquid wastes and sludges. Impoundment is usually considered a terminal disposal method only when contained water is removed by evaporation from the pond and the residues are landfilled in place.

As with landfills, the most important consideration is protection of the adjacent natural water; however, in contrast to landfills, migration of toxic components is not inhibited by adsorption by solid wastes or soil, and the impermeability of the containing pond or basin is of even greater importance.

b. Aqueous Wastes——Open ponds or basins are frequently used for the storage of aqueous wastes that are not amenable to biological treatment or acceptable for discharge to receiving waters. These wastes (e.g., brines) frequently contain high concentrations of dissolved or suspended solids and are often permitted to evaporate to dryness. This is not considered as an acceptable practice if the wastes contain significant concentrations of VOC; unless there is significant biological activity, essentially all the contained VOC will eventually result in secondary emissions.

c. Liquid Organic Wastes——Open ponds or basins can be used only for temporary storage of liquid organic wastes. Basically, the only manner in which liquid organic wastes can be terminally disposed of by impoundment is from the evaporation of the contained organic compounds, a totally unacceptable practice.

d. Solid Wastes——Impoundment basins are frequently used for the storage and drying of biological and chemical sludges. Activated sludge, as discharged from a biological waste treatment plant, will typically contain 95 to 98% water. Sludge is usually dewatered to produce a cake with a solids concentration of 12 to 40% before final disposal by landfill or incineration. When sludge is dried by evaporation of the contained water in an open basin, secondary emissions may occur as the result of the concurrent evaporation of VOC contained in the sludge.

3. Deep-Well Injection

a. General——The underground injection of liquid wastes into permeable rock formations isolated from potable water and mineral-bearing strata is in some cases the only safe method for disposing of certain indestructible, nonconvertible, or otherwise hard-to-treat hazardous substances.[2] The use of deep-well injection is generally selected only after all reasonable alternative disposal methods have been evaluated and found to be less desirable in terms of environmental protection and dependability.

Secondary emissions resulting from actual deep-well injection operations are generally minimal; however, preinjection storage or pretreatment operations may result in significant secondary emissions. The most prevalent pretreatment requirements are those aimed at preventing the injection wells from being plugged by solids that are either suspended in the liquid wastes or are formed by precipitation when dissolved waste components react with the well formation fluid. The secondary emissions result primarily from the evaporation of contained organics that occurs during the required preinjection treatment operations (e.g., neutralization, precipitation, solid/liquid separation).

b. Aqueous Waste——Deep-well injection of aqueous wastes is primarily used when the wastes contain high concentrations of inorganic compounds, including acids such as sulfuric, hydrochloric, and phosphoric; bases, such as sodium hydroxide; and salts, such as sodium chloride, sodium sulfate, aresenic sulfide, ammonium bisulfate, sodium bromide, and calcium carbonate.

c. Liquid Wastes——Organic chemicals that are disposed of by deep-well injection include acids, such as maleic, formic, adipic, cresylic, salicylic, and acetic; alcohols, such as methanol, tertiary butanol, phenol, and isopropanol; solvents, such as acetone, toluene, xylene, formaldehyde, ethylbenzene, benzaldehdye, and methyl ethyl ketones; and other compounds, such as sodium naphthenate, sodium cresylate, calcium and sodium acetate, and large molecular structures, such as styrene polymers and various polymeric resins.

d. Solid Wastes——Not applicable; solids generally cause well-plugging problems.

G. DISCHARGE TO NATURAL WATERS

1. Introduction

The primary concern stemming from the discharge of wastes to natural waters (including the dilution of aqueous effluents and the ocean dumping of containerized or bulk wastes) is with the effect of the wastes on the water quality. Generally, if pretreatment methods are acceptable from the standpoint of water quality, secondary emissions will be minimal.

2. Dilution of Aqueous Effluents

a. Aqueous Wastes——The prevailing method for the terminal disposal of aqueous wastes is by discharge and dilution in natural receiving waters. Generally, if pretreatment is acceptable from the standpoint of the effect of the wastes on the water quality, secondary emissions are minimal.

b. Liquid Waste——The direct discharge of liquid organic wastes into natural receiving waters is never an acceptable practice.

c. Solid Wastes——The discharge of solid wastes (with the exception of deep-ocean dumping) is not an acceptable practice.

3. Ocean Dumping

a. Aqueous Wastes——Deep-ocean dumping of aqueous wastes is not generally applicable.

b. Liquid Wastes——Ocean dumping of bulk liquid organic wastes is not an acceptable practice. Deep-ocean dumping of containerized, stabilized, or encapsulated liquid wastes, although possibly undesirable from the standpoint of long-term water quality, probably results in minimal secondary emissions.

c. Solid Wastes——Secondary emissions are minimal.

H. REFERENCES*

1. R. L. Huddleston, "Solid-Waste Disposal: Landfarming," Chemical Engineering 86(5), 119—124 (Feb. 26, 1979).
2. M. E. Smith, "Solid-Waste Disposal: Deepwell Injection," Chemical Engineering 86(8), 107—112 (Apr. 9, 1979).

*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

IV. EMISSIONS

A. INTRODUCTION

Secondary emissions are estimated to account for 2 to 5% of the total VOC emissions from the SOCMI in 1978. The primary secondary emission sources and estimates of the corresponding total secondary emissions for 34 of the most significant organic chemicals produced by the SOCMI are given in Table IV-1. The data in Table IV-1 were extracted from the Emissions Control Options for the SOCMI Product Reports (on file at EPA, ESED, Research Triangle Park, NC). The product chemicals listed (same as in Table II-2) account for less than 10% of the total number of chemicals produced but account for more than 70% of the total quantity produced.

The estimates of secondary emissions listed in Table IV-1 are based on very limited data. Secondary emissions are, in general, difficult to measure. The estimates given were based primarily on the physical and chemical properties of the primary organic waste components and on estimates of the quantities and the composition of wastes. A review of the pertinent literature on secondary emissions and estimating methods is given in Appendix A.

One of the major difficulties in sampling for secondary VOC emissions results from the dispersion of secondary VOC emissions in the ambient air. A promising technique for assessing the effect of dispersion on secondary VOC emissions has been tried in two studies, one on fugitive emissions[1] and the other on secondary emissions.[2] The technique involves sampling upwind and downwind of the emission source at different horizontal and vertical points in the secondary-VOC-emission plume. Dispersion mathematics can then be used to calculate the emission rate of a hypothetical source that would be necessary to produce the plume.

Following is a brief discussion of emissions from the sources described in Sect. III. The bulk of secondary emissions (50 to 90%) are estimated to result from the handling, storage, pretreatment, and terminal treatment (primarily biological treatment) of aqueous wastes. Other sources of major significance include landfilling, surface impoundment, and incineration of liquid and solid wastes. Only the sources of major significance are discussed in detail in this section; this is also true in Sects. V ("Applicable Control Methods") and VI ("Impact Analysis").

Table IV-1. SOCMI Secondary Emission Sources and Estimated Emissions

Product	Primary Process	Estimated 1978 Production (Gg/yr)	Type of Waste	Secondary Emission Source	Estimated Secondary Emissions	
					Ratio (kg/Mg)[a]	Rate (Mg/yr)
Acetaldehyde	Ethylene oxidation	450	Aqueous	Biotreatment or deep-well	b	b
			Liquid	Incineration or deep-well	b	b
Acetone/phenol	Cumene	900	Aqueous	Biotreatment	1.6	1300
Acetic anhydride	Acetic acid pyrolysis	680	Aqueous	Biotreatment	b	b
			Solid	Landfill or incineration	b	b
Acrylic acid and esters	Propylene oxidation	410	Aqueous	Biotreatment	0.05	
			Liquid	Incineration	0.001	
			Solid	Incineration		
Total					0.051[c]	40[c]
Acrylonitrile	Propylene oxidation	815	Aqueous	Holding pond, deep-well	5.34	
			Liquid	Incineration	0.36	
Total					5.71	4650
Adipic acid	Nitric acid oxidation	855	Aqueous	Holding pond, deep-well	Neg.	Neg.

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[a] kg of emission per Mg of product produced.

[b] Information not available.

[c] Does not include emissions resulting from H_2SO_4 recovery.

Table IV-1. (Continued)

Product	Primary Process	Estimated 1978 Production (Gg/yr)	Type of Waste	Secondary Emission Source	Estimated Secondary Emissions	
					Ratio (kg/Mg)[a]	Rate (Mg/yr)
Alkylbenzene	Olefins	250	Aqueous	Deep-well injection	0.033	3.0
			Solid	Landfill		
	Chlorination		Aqueous	Biotreatment	0.253	45.0
			Liquid	Incineration		
			Solid	Landfill		
Total						48
Butadiene	n-Butane dehydrogenation	260	Aqueous	Biotreatment	0.150	40
			Solid	Incineration		
	Oxidative dehydrogenation	265	Aqueous	Biotreatment	0.240	64
			Solid	Incineration		
	By-product of ethylene manufacture	975	Aqueous	Biotreatment	0.150	146
			Solid	Incineration		
Total						250
Caprolactam	Cyclohexanone	400	Aqueous	Biotreatment		
			Liquid	Incineration		

Table IV-1. (Continued)

Product	Primary Process	Estimated 1978 Production (Gg/yr)	Type of Waste	Secondary Emission Source	Estimated Secondary Emissions	
					Ratio (kg/Mg)[a]	Rate (Mg/yr)
Chlorobenzenes	Benzene chlorination	220	Aqueous	Biotreatment	0.28	62
			Solid	Landfill	Neg.	Neg.
Total						62
Chloromethanes	Methane chlorination	930	Aqueous	Disposal	0.13	120
			Liquid	Incineration		
Cumene	Phosphoric acid catalyst	968	Aqueous	Biological treatment	0.008	8
			Solid	Landfill	b	b
	Aluminum chloride catalyst	289	Aqueous	Biological treatment	0.23	67
Total						75
Cyclohexanol/ cyclohexanone	Cyclohexane	1,012	Aqueous	Biological treatment	0.0911	92
			Liquid	Incineration		
	Phenol hydrogenation	178	Aqueous	Biological treatment	Neg.	Neg.
			Liquid	Not indicated	Neg.	
Total						92

Table IV-1. (Continued)

Product	Primary Process	Estimated 1978 Production (Gg/yr)	Type of Waste	Secondary Emission Source	Estimated Secondary Emissions Ratio (kg/Mg)[a]	Estimated Secondary Emissions Rate (Mg/yr)
Ethanolamines	Ethylene oxide and ammonia	165	Aqueous	Biotreatment	b	b
			Liquid	Landfill, incineration, sales	b	b
Ethylene	Ethane/propane feed	6,100	Aqueous	Phase separation and biotreatment	0.02	122
			Solid	Landfill	Neg.	b
	Naphtha feed	3,000	Aqueous	Phase separation and biotreatment	0.04	122
			Solid	Landfill	Neg.	b
	Gas oil feed	3,000	Aqueous	Phase separation and biotreatment	0.07	214
			Solid	Landfill	Neg.	
Total						458
Ethylbenzene/styrene	Benzene alkylation dehydrogenation	3,200	Aqueous		0.079	253
			Liquid Solid	Incineration	0.009	29
Total					0.088	282

Table IV-1. (Continued)

Product	Primary Process	Estimated 1978 Production (Gg/yr)	Type of Waste	Secondary Emission Source	Estimated Secondary Emissions	
					Ratio (kg/Mg)[a]	Rate (Mg/yr)
Ethylene dichloride/vinyl chloride	Direct chlorination	4,900	Aqueous	Biotreatment	0.027	130
			Liquid and/or solid	Incineration	0.095	470
Total					0.122	600
Ethylene glycol	Ethylene oxide hydration	1,960	Aqueous	Biotreatment	0.772	1513
			Liquid	Incineration of landfill	Neg.	b
Total						1513
Ethylene oxide	Ethylene oxidation (air)	1,460	Liquid	Incineration	0.0116	17
			Solid	Landfill	Neg.	
	Ethylene oxidation (oxygen)	729	Liquid	Incineration	0.013	10
			Solid	Landfill	Neg.	
						27

Table IV-1. (Continued)

Product	Primary Process	Estimated 1978 Production (Gg/yr)	Type of Waste	Secondary Emission Source	Estimated Secondary Emissions Ratio (kg/Mg)[a]	Estimated Secondary Emissions Rate (Mg/yr)
Formaldehyde	Metallic silver catalyst	2,250	Aqueous	Biotreatment	0.01	23
	Metal oxide catalyst	750	Aqueous	Biotreatment	0.05	38
Total						61
Glycol ethers	Reaction of alcohols with ethylene and/or propylene oxide	281	Aqueous	Biotreatment	0.0019	0.5
			Liquid	Not specified	0.025	7.0
Total						7.5
Maleic anhydride	Benzene oxidation	135	Aqueous	Handling and biotreatment	0.05	6.8
			Liquid	Incineration		
			Solid	Catalyst reclamation	Neg.	Neg.
Total						6.8
Methanol	Low pressure	335	Aqueous	Biotreatment	0.00044	
			Liquid	Incineration	0.00006	
Total					0.0005	1.7

Table IV-1. (Continued)

Product	Primary Process	Estimated 1978 Production (Gg/yr)	Type of Waste	Secondary Emission Source	Estimated Secondary Emissions Ratio (kg/Mg)[a]	Estimated Secondary Emissions Rate (Mg/yr)
Methyl methacrylate	Acetone cyanohydrin	398	Aqueous	Biological treatment	b	b
			Liquid	Sulfuric acid recovery	b	b
			Solid	Incineration or landfill	b	b
Nitrobenzene	Benzene nitration	434	Aqueous	Sulfuric acid recovery	0.33	143
				Wastewater treatment		
Perchloroethylene/ trichloroethylene	Oxychlorination	300	Aqueous	Biotreatment	b	b
		135	Liquid and/or solid	Incineration	b	b
Propylene oxide	Chlorohydronation	500	Aqueous	Biotreatment	2.6	2100
	i-Butane peroxidation[d]	280	Aqueous	Biotreatment		
			Liquid	Incineration		
	Ethylbenzene peroxidation	130	Aqueous	Biotreatment		
			Liquid	Incineration		
			Solid	Landfill		
Total					2.6	2100

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[d] t-Butanol produced as co-product.

Table IV-1. (Continued)

Product	Primary Process	Estimated 1978 Production (Gg/yr)	Type of Waste	Secondary Emission Source	Estimated Secondary Emissions	
					Ratio (kg/Mg)[a]	Rate (Mg/yr)
Terephthalic acid (crude)	Air oxidation	1,989	Aqueous	Biotreatment	0.004	8
			Liquid	Incineration	0.006	12
Total						20
1,1,1-Trichloro-ethane	Vinyl chloride	310	Aqueous	Biotreatment	0.001	0.62
			Liquid/ solid	Incineration	<0.001	
	Ethane	18	Aqueous	Biotreatment	0.001	0.04
			Liquid/ solid	Incineration	<0.001	
Total						0.66

B. PHYSICAL SEPARATION METHODS

1. Steam Stripping

a. Aqueous Wastes——Steam stripping is frequently used to control secondary emissions from subsequent treatment operations. Secondary emissions primarily result from venting noncondensed gas from the stripper condenser (primarily air) and are generally relatively low.

b. Liquid Organic Wastes——Steam stripping is not generally used for the treatment of liquid organic wastes.

c. Solid Wastes——As with aqueous wastes, stream stripping, or purging, of solids is frequently used to reduce secondary emissions from subsequent treatment or disposal operations. Emissions resulting from the venting of noncondensable gases (air) are relatively low.

2. Conventional Distillation

a. Aqueous Wastes——Conventional distillation is not generally used for the treatment of aqueous wastes unless the concentration of organics is significant. As with steam stripping, emissions chiefly result from the venting of noncondensable gases. Secondary emissions are relatively minor.

b. Liquid Wastes——Although conventional distillation of organic liquids is a common process operation, it is infrequently used for the treatment of wastes. Secondary emissions are minor and result from the venting of noncondensable gases.

c. Solid Wastes——Not applicable.

3. Liquid-Liquid Phase Separation/Emulsion Breaking

a. Aqueous Wastes——The most significant emissions occur when open-topped and atmospherically vented separation vessels (e.g., API oil/water separators, plate separators) are used, when the organic phase is the upper layer, and when the vapor pressures of the organic compounds are significant.

b. Liquid Wastes——The comments concerning emissions from aqueous wastes also apply to liquid wastes.

c. Solid Wastes——Not applicable.

4. Solid-Liquid Separation

1. Aqueous Wastes——The solid-liquid separation operations used in the treatment of aqueous wastes are usually integral steps in biological wastewater treatment processes (i.e., sedimentation, clarification, thickening) and are significant sources of secondary emissions. A primary clarifier is included in a model wastewater treatment plant using the continuous activated sludge system (CAS) described in Sect. IV-E-1-b. Sample calculations for estimating emissions of VOC from soluble aqueous wastes in open-topped vessels are given in Appendix B. This type of calculation is applicable to the estimation of secondary emissions from all aqueous waste treatment and storage operations occurring in open-topped vessels in which the primary emission mechanism is the vaporization of soluble organics (i.e., solid-liquid separation, aeration, neutralization, impoundment).

b. Liquid Wastes——Secondary emissions resulting from the separation of solids from liquid organic wastes are relatively minor.

c. Solid Wastes——Discussed above.

C. CHEMICAL TREATMENT

1. Neutralization

a. Aqueous Wastes——The neutralization/equalization of aqueous wastes, frequently a pretreatment step to biological wastewater treatment and usually occurring in open-topped basins or vessels, may result in significant secondary emissions. Secondary emissions, which result chiefly from the vaporization of contained organics, may be estimated by the methods shown in the sample calculations (Appendix B).

b. Liquid Wastes——Not generally applicable.

c. Solid Wastes——Not generally applicable.

2. Precipitation and Coagulation

a. Aqueous Wastes——Significant secondary emissions may result from precipitation/coagulation operations conducted in open-topped vessels. The emissions, which result chiefly from the vaporization of contained organics, may be estimated by the methods shown in the sample calculations (Appendix B).

b. Liquid Wastes——Not generally applicable.

c. Solid Wastes——Secondary emissions from solid wastes generated by precipitation/coagulation operations occur in solid-waste terminal treatment or disposal operations (e.g., incineration, landfilling) (see Sects. IV-D and F).

3. Chemical Oxidation

a. Aqueous Wastes——Chemical oxidation processes are used relatively infrequently and generally take place in enclosed or pressurized vessels. Secondary emissions are relatively insignificant.

b. Liquid Wastes——Not generally applicable.

c. Solid Wastes——Not generally applicable.

D. THERMAL DESTRUCTION

1. Aqueous Wastes

As thermal destruction or incineration is not generally used for the disposal of aqueous wastes, secondary emissions are relatively insignificant.

2. Liquid Wastes

Combustion in incinerators or boiler combustion chambers is widely used in the SOCMI for the terminal disposal of large quantities of liquid organic wastes. Combustion efficiencies in excess of 99% can as a rule be readily attained if the recommended residence time and combustion zone temperature requirements are met. Secondary emissions resulting from incomplete oxidation of organics are generally relatively low compared to emissions from alternative terminal treatment methods. Although the concentration of VOC in the vented flue gas is usually very low, the quantity of contained organics vented may be significant because of the extremely large quantities of flue gas vented. Estimates of secondary emissions resulting from the combustion of liquid organic wastes were generally based on an assumed VOC removal efficiency of 99%.

3. Solid Wastes

Combustion requirements necessary for the satisfactory thermal destruction of solid wastes are generally more stringent than those for liquid wastes. Incinerators designed for specific waste profiles are generally required; however, at suitable conditions, destruction efficiencies for organics in solid wastes are also usually 99% or better.

E. BIOLOGICAL TREATMENT

1. Aqueous Wastes

a. Introduction——Emissions resulting from the handling and treatment of aqueous wastes or wastewater probably represent 50 to 90% of the uncontrolled secondary emissions from the SOCMI, based on the estimates described in the following sections. The bulk of the wastewater generated by the industry is treated biologically, with the resulting secondary emissions occurring during the separate operations involved in biological treatment and any necessary pretreatment. Some of the separate unit operations that are normally included in biological treatment and pretreatment (e.g., liquid/solid separation, neutralization) are described in Sect. II.

b. Model Plants——A theoretical order-of-magnitude estimate of total SOCMI uncontrolled secondary VOC emissions from wastewater was made based on 30 high-volume chemicals with available wastewater data[3—7] and on the wastewater secondary VOC emission estimation models of Mackay[8] and Thibodeaux[9] applied to the wastewater data and the model wastewater treatment plant shown in Fig. IV-1 and detailed in Table IV-2. Actual wastewater treatment plants are designed to meet individual requirements and may differ significantly from the model.

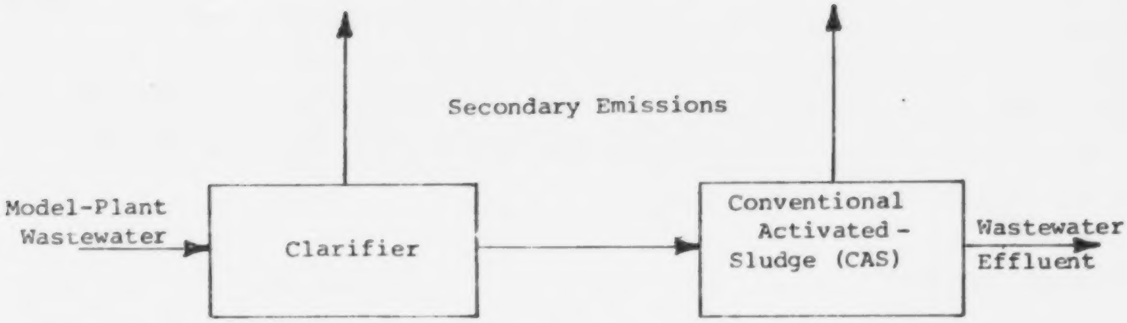

Fig. IV-1. Uncontrolled Secondary VOC Emissions from Model-Plant Wastewater (Total, 1060 Mg of VOC Emissions Per Year)

Table IV-2. Parameters for Model-Plant Wastewater Treatment System

Primary clarifier	
Depth (m)	3
Surface area (m^2)	700
Retention time (hr)	3
Activated-sludge system (CAS)	
Depth (m)	6
Surface area (m^2)	6300
Air flow (m^3/min)	612

The model wastewater treatment system used in the analysis consists of a clarifier and activated sludge system sized according to industrial practices for the wastewater flow from a model chemical production plant (MCPP). The operational parameters for the MCPP, given in Table IV-3, are based on production-weighted averages for the 30 chemicals with available wastewater data.[3—7]

c. Emissions——An estimate of total uncontrolled secondary wastewater emissions resulting from the production of 30 high-volume chemicals is summarized in Table IV-4. The average uncontrolled secondary VOC wastewater emission factor for the 30 chemicals is estimated as 650 g of VOC per Mg of product. Applying this estimated secondary emission factor to the 1978 estimated industry production of 100,000 Gg results in an estimate of 65 Gg/yr for uncontrolled secondary emissions from SOCMI wastewater. Because the 30 chemicals represent 55 wt % of 1978 SOCMI production, this is considered to be reasonable order-of-magnitude estimate for the industry wastewater emissions.

It should be emphasized that, although the estimate of total emissions given in Table IV-4 is probably of reasonable accuracy, the estimates of secondary emission rates shown for the individual products are each based on a single organic component in the wastewater (the primary product) and may be significantly in error. The estimates of secondary emissions from the product reports (summarized in Table IV-1) cannot be compared with those from Table IV-4 as the tables are based on the following differences in criteria: (1) Table IV-1 is for total secondary emissions; Table IV-4 is for emissions from wastewater only; (2) Table IV-1 is for uncontrolled emissions; Table IV-4 estimates the actual current emissions.

A discussion of the estimating procedures used is presented in Appendix B. The criteria on which the estimates were based, sample calculations, and summaries of the calculations are given in Appendix C.

2. Liquid Organic Wastes——Biological treatment is not generally used for liquid wastes containing more than 1% organic compounds.

3. Solid Wastes——Not generally applicable.

Table IV-3. Operational Parameters for Model Chemical Production Plant

Production (Gg/yr)	1,650
Wastewater flow (m^3/day)	17,000
Wastewater COD content (mg/liter)	3,000
Wastewater chemical content (mg/liter)	1,360
Amount of chemical in wastewater leaving plant (Gg/yr)	8.44
Henry's-law constant, M_{xi}, for chemical in wastewater	25
Molecular weight of chemical	58

Table IV-4. Estimated Order-of-Magnitude Uncontrolled-Secondary-Emission Wastewater Factors for 30 Organic Chemical Products

Chemical	Approximate 1978 Production (Gg/yr)	Secondary VOC Emission Factor (SE_f)*	Secondary VOC Emission Rate (Gg/yr)
Ethylene	11,800		2.6
Ethylene dichloride	4,900		12.2
Styrene	3,200	67	0.2
Methanol	2,900	2	0
Ethylbenzene	3,700	16	0
Vinyl chloride	3,100	876	2.7
Ethylene oxide	2,200	1143	2.5
Ethylene glycol	1,900	0	0
1,3-Butadiene	1,500	959	1.4
Dimethylterephthalate	1,300	3	0
Cumene	1,500	0	0
Acetic acid	1,200	0	0
Cyclohexane	1,100	0	0
Phenol	1,200	0	0
Chlorinated methanes	900	2246	2.0
Isopropyl alcohol	800	31	0
Acetone	900	1575	1.4
Propylene oxide	900	2623	2.4
Acetic anhydride	700	260	0.2
Acrylonitrile	800	7283	5.8
Ethanol	600	201	0.1
Vinyl acetate	800	10	0
Terephthalic acid (crude)	2,000	0	0
Adipic acid	800	0	0
t-Butanol	600	2868	1.7
Acetaldehyde	500	910	0.5
Cyclohexanol/cyclohexanone	1,000	6	0
Phthalic anhydride	1,000	0	0
Adiponitrile	400	0	0
Caprolactam	400	0	0
Total	54,600		35.7

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*g of secondary VOC emissions per Mg of product produced.

F. TERMINAL STORAGE

1. Landfill

a. Aqueous Waste——Not generally applicable.

b. Liquid Wastes——Significant secondary emissions are believed to result from the landfilling of liquid organic wastes, primarily from those with significant vapor pressures that are not containerized or stabilized before landfilling. Actual emission data are extremely scarce.

c. Solid Wastes——The comments concerning liquid wastes (Sect. IV.F.1.b) also apply to solid wastes.

d. Comparison of Estimated Secondary VOC Emissions from a Wastewater Treatment System and a Chemical Landfill——Because of the scarcity of data for secondary emissions resulting from the landfilling of liquid and solid wastes, a theoretical sensitivity analysis was made to permit an order-of-magnitude comparison between the potential emissions from wastewater treatment and those from landfilling operations. The sensitivity analysis was performed for hexachlorobenzene (HCB), p-dichlorobenzene (DCB), benzene (Bz), acetone, and acetic acid. These model chemicals were chosen because they represent a wide range of volatilities and physical properties. The secondary VOC emission estimation was performed by using the Mackay,[8] Thibodeaux,[9] and Farmer[10] estimation models (see Appendix D). The operational parameters for the model landfill are given in Table IV-5.

The organically contaminated wastewater, liquid organic wastes, and solid organic wastes generated are treated as single-component wastes with average physical and chemical properties. The results of the analysis are summarized in Table IV-6, and the bases and calculations for the analysis are given in Appendix C.

The sensitivity analysis for wastewater treatment and landfill summarized in Table IV-6 suggests that for low-water-soluble, low-vapor-pressure chemicals most of the secondary VOC emissions of the chemical will be from wastewater treatment. The analysis also suggests that the secondary VOC emissions from landfill compared with wastewater emissions increase for low-water-soluble, high-vapor-pressure chemicals such as benzene. Comparison of the secondary VOC

Table IV-5. Parameters for Model-Plant Landfill

Solid waste (Gg/yr)	4.2
Waste bulk density (g/cm^3)	1.0
Landfill area (m^2 per year)	4047
Landfill soil moisture	Dry
Depth of soil cover (m)	0.6

Table IV-6. Comparison of Estimated Secondary VOC Emissions from a Wastewater Treatment Plant with Those from a Chemical Landfill at a Model Chemical Production Plant

Source	Secondary VOC Emissions (Mg/yr)				
	HCB	DCB	Benzene	Acetone	Acetic Acid
ndfill[a]	3.2×10^{-4}	12	840	1675	88
del wastewater treatment system					
Clarifier	2.4×10^{-3}	46.1	1488	186	8.4
Activated-sludge system					
Easy to biodegrade		42.4[b]	2020	12	0.4
Difficult to biodegrade	3.6×10^{-2}	447[b]			
stewater totals	3.8×10^{-2}	88—493	3508	198	8.8

* * * * *

tio of wastewater emission rate to sanitary landfill emission rate	119	7—41	4.2	0.1	0.1

ased on 4047 m^2 per year of sanitary landfill used.

CB was estimated both ways to show the relative importance of biodegradability on the econdary VOC emission rates from an activated-sludge system.

emissions from liquid chemicals that have higher vapor pressures and are more water stable, such as acetone and acetic acid, suggests that more of the secondary VOC emissions for these chemicals will be from landfill than from wastewater.

The analysis described in Appendix C for landfill is a worst-case estimate based on dry soil. In actual landfill situations in which there are moist soil, biological decomposition, and some downward percolation of water, the secondary VOC emissions for highly water soluble chemicals such as acetone and acetic acid will be lower than the values shown.

2. Surface Impoundment

a. Aqueous Wastes——A preliminary sensitivity analysis, similar to that shown in Table IV-6, was done for the secondary VOC emissions from landfill and surface impoundments. The analysis suggested that the two most important physical property indicators, relative to secondary VOC emission potential, are the vapor pressure and the aqueous solubility of the waste chemicals. The analysis also suggested that secondary VOC emissions from surface impoundments are potentially significant relative to landfill secondary VOC emissions.

The calculational models used for the sensitivity analysis were particularly sensitive to the average SOCMI vapor pressures assumed for the wastes being put into landfill and for the aqueous solubilities assumed for the wastes being put into surface impoundments. Since no data were available on the average vapor pressure and average aqueous solubilities of SOCMI wastes going to landfill and to surface impoundments, no meaningful estimate of secondary VOC emissions from these sources could be made.

b. Liquid Wastes——The storage of liquid organic wastes that have significant vapor pressures in open basins is not an acceptable practice.

c. Solid Wastes——No information available.

G. DISCHARGE TO NATURAL WATERS

1. Dilution of Aqueous Effluents

a. Aqueous Wastes——Generally, if pretreatment is acceptable from the standpoint of the effect of the wastes on water quality, secondary emissions are minimal.

b. Liquid Wastes——The discharge of liquid organic wastes into natural receiving waters is never an acceptable practice.

c. Solid Wastes——The discharge of solid wastes (with the exception of deep-ocean dumping of containerized wastes) is not an acceptable practice.

2. Ocean Dumping

a. Aqueous Wastes——Not generally applicable.

b. Liquid Waste——The ocean dumping of bulk liquid organic wastes in not an acceptable practice. The ocean dumping of containerized or stabilized liquid wastes probably results in minimal secondary emissions.

c. Solid Wastes——Secondary emissions are minimal.

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

V. APPLICABLE CONTROL METHODS

A. INTRODUCTION

The primary categories of methods by which secondary emissions can be controlled include (1) waste source control——the elimination or reduction of aqueous, liquid, or solid wastes or the reduction in the concentration of VOC in the wastes through changes in the waste generating processes; (2) resource recovery——the reduction in the quantity or VOC concentration of wastes requiring terminal treatment or disposal through the addition of recovery operations between the waste generating processes and terminal treatment; the recovered organics may be recycled, sold as by-products, or burned (providing fuel value); (3) alternate disposal——the reduction of secondary emissions by the use of alternate terminal treatment or disposal methods, which generate lower secondary emissions; and (4) add-on controls——the reduction of secondary emissions released to the atmosphere by the addition of controls to waste treatment and disposal operations.

Table V-1 is a summary of specific control methods within these categories and of the secondary emission sources where they are applicable; however, only the more prevalent combinations of control methods and significant emission sources are discussed in the text. As with the emission sources, the general categories within which specific control methods fall are not always clear-cut, and they tend to overlap to some extent. It may also be noted that operations which are considered as secondary emission sources may also occur as emission control methods. Following is a discussion of the specific control methods. The estimated ranges of emission reductions provided by the most prevalent control methods are given in Table V-2.

B. WASTE SOURCE CONTROL

1. Introduction

Secondary emissions can frequently be reduced through changes in the waste sources or waste generating processes. These changes can be effected by reducing the quantity of wastes generated, by reducing the concentration of VOC in the wastes, or by altering the waste characteristics to make the wastes amenable to alternative disposal methods that emit less secondary emissions. Because a reduction

Table V-1. Applicable Control Methods

	Waste Source Control								Resource Recovery						Alternative Terminal Treatment				Add-On Controls				
Secondary Emission Source Operation	Alternative Waste Source Processes	Alternative Raw Materials	Improved Separations	Internal Recycle	Leak Elimination	Reduced Water/Steam Use	Prevent Water/Organic Contact	Improved Process Control	Steam Stripping	Conventional Distillation	Adsorption	Extraction	Emulsion Breaking	Membrane Separations	Incineration	Deep-Well Disposal	Landfill	Advanced Biological Treatment	Covers	Carbon Adsorption	Thermal Destruction	Stabilization	Refrigerated Condenser
Physical separation																							
Distillation/steam stripping	X	X	X	X		X	X	X					X							X	X		X
Liquid/liquid phase separation	X	X	X	X	X	X	X	X	X										X	X	X		X
Solid/liquid separation	X	X	X	X	X	X	X	X	X						X	X	X		X	X	X		X
Chemical treatment																							
Neutralization	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X		
Precipitation/coagulation	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X	X		X	X	X		X
Chemical oxidation	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X		X	X		X
Thermal destruction																							
Incineration	X	X	X	X	X			X		X	X	X	X	X		X		X					
Biological treatment																							
Activated sludge reaction	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X		X	X	X		
Clarification	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X		X	X	X		
Thickening/dewatering	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X		X	X	X		
Terminal storage																							
Landfill	X	X	X	X	X			X	X	X	X	X	X	X	X	X		X	X			X	
Surface impoundment	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X		X
Deep-well disposal	X	X	X	X	X	X	X	X										X					
Discharge to natural waters	X	X	X	X	X	X	X	X										X					
Ocean dumping	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			X		

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Table V-2. Secondary VOC Emission Reductions by Various Control Techniques or Methods*

Control Option	Reduction Range (%)
Organically contaminated wastewater	
Source control	10—90
Resource recovery	10—90
Immiscible organic cover	50—90
Floating plastic spheres	70—90
Floating plastic cover	>99
Collection/carbon adsorption	95—>99
Collection/thermal destruction	>99
Organic liquid and solid	
Landfill	
Soil cover	75—99+
Plastic cover	>99
Surface impoundment	
Immiscible organic cover	50—90
Floating plastic spheres	70—90
Floating plastic cover	>99

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[*] Based on the limited data available plus engineering experience and judgement.

in the quantity of waste or VOC concentration almost always results in a corresponding reduction in VOC emissions, waste source control is effective in reducing emissions from almost all secondary sources.

2. Alternative Waste Source Processes or Process Steps

a. Aqueous Wastes——Secondary emissions from alternative processes or process steps by which the same product is made are often significantly different. Although the use of an alternative process is often not feasible as a secondary emission control method in an existing plant, potential secondary emissions should be considered in process selection for a new facility.

b. Liquid Wastes——See Sect. V-B-2-a.

c. Solid Wastes——See Sect. V-B-2-a.

3. Alternative Raw Materials

a. Aqueous Wastes——Frequently the use of alternative raw materials or raw materials with lower concentrations of impurities or diluents will result in reduced quantities of wastes generated or reduced VOC concentration.

b. Liquid Wastes——See Sect. V-B-3-a.

c. Solid Wastes——See Sect. V-B-3-a.

4. Improved Separations

a. Aqueous Wastes——The concentration of VOC in aqueous wastes is frequently dependent on the efficiency of physical separation steps (e.g., distillation, phase separation) within the source processes. Improvement in separation efficiency can result in significant reduction in the VOC concentration of the wastes and a corresponding reduction in secondary emissions.

b. Liquid Wastes——Generally not significant.

c. Solid Wastes——Generally not significant.

5. Internal Recycle

a. Aqueous Wastes——The quantity of wastes discharged can frequently be reduced with modifications to source processes that permit the internal recycle of waste streams with a corresponding reduction in makeup requirements. The treatment of aqueous wastes necessary to permit recycle to the process may be less demanding than the treatment required for acceptable discharge and may result in reduced secondary emissions.

b. Liquid Wastes——See Sect. V-B-5-a.

c. Solid Wastes——See Sect. V-B-5-a.

6. Leak Reduction

a. Aqueous Wastes——The reduction of small and intermittent leaks of organics from process equipment, storage tanks, and piping can often significantly reduce secondary emissions, as well as fugitive emissions.

Leaks in heat exchanger tubes often contribute to increased aqueous wastes and/or increased VOC concentration. The introduction of water into process streams through leaks in heat exchanger tubes eventually results in increased aqueous wastes. The leakage of organics into cooling water results in increased VOC concentration in wastewater or in increased fugitive emissions from cooling towers. Frequent systematic inspection and maintenance and effective equipment specifications are usually the most effective means of minimizing leaks. Monitoring organic levels in process cooling wastewater can be used to indicate the presence of process leaks.

b. Liquid Wastes——See Sect. V-B-6-a.

c. Solid Wastes——Not generally applicable.

7. Reduction of Water/Steam Usage

a. Aqueous Wastes——Most of the water or steam directly introduced into source processes is eventually discharged as aqueous wastes. Usage can frequently be reduced with the systematic examination of requirements and actual usage.

b. Liquid Wastes——Not applicable.

c. Solid Wastes——Not applicable.

8. Prevention of Water/Organic Contact

a. Aqueous Wastes——The quantity of aqueous wastes and/or the concentration of VOC can often be reduced by eliminating operations that require the direct contact of organic process streams with water that is eventually discharged as wastewater. This is most frequently accomplished by the use of heat exchangers instead of direct water contact operations.

b. Liquid Wastes——Not applicable.

c. Solid Wastes——Not applicable.

9. Improved Process Control

a. Aqueous Wastes——The reduction in process upsets and improved control of process parameters can result in significant reductions in process wastes and the corresponding secondary emissions. Improvements are generally attained with better process control equipment, improvement in control application, and improved training of operating personnel.

b. Liquid Wastes——See Sect. V-B-9-a.

c. Solid Wastes——See Sect. V-B-9-a.

RESOURCE RECOVERY

Introduction

The recovery of organic raw materials, products, or by-products from waste streams prior to terminal treatment is often an effective method of reducing VOC concentration and the corresponding secondary emissions. Most resource recovery operations utilize physical separation methods, as described in Sects. II and III. Some recovery operations are relatively complex and may require reactions, as well as separation steps. Resource recovery may not be economically feasible for streams containing very low VOC concentrations or for streams containing a number of organic components that are not usable as mixtures and that cannot be readily separated.

When applicable, the primary advantage of resource recovery as a method for controlling emissions is that the value of the recovered materials will usually at least partially offset the cost of control. Frequently a net profit can be realized. In addition to the recovery of products, raw-material and salable by-product recovery operations may be used to concentrate organic wastes present in aqueous wastes, permitting the organic wastes to be burned as fuel with positive heating value. Recovery operations are primarily used for treating aqueous wastes, and the resulting reductions in secondary emissions occur largely in biological treatment and pretreatment.

Steam Stripping

Aqueous Wastes——Steam stripping is used primarily to recover VOC from aqueous wastes.

Liquid Wastes——Not generally applicable.

Solid Wastes——The steam stripping of solids, although used in reducing VOC content, is seldom used for recovery.

Conventional Distillation

Aqueous Wastes——Not generally applicable.

b. Liquid Wastes——Conventional distillation as a recovery method is chiefly used for treating liquid organic wastes for separating usable products, by-products, or raw materials.

c. Solid Wastes——Not generally applicable.

4. Adsorption

a. Aqueous Wastes——Adsorption, usually with activated carbon, can effectively remove organic compounds even when present at very low concentrations from aqueous wastes. As discharge requirements for wastewater become increasingly stringent, activated carbon adsorption is being used more widely both for resource recovery and for final terminal treatment.

b. Liquid Wastes——Not generally applicable.

c. Solid Wastes——Not generally applicable.

5. Solvent Extraction

a. Aqueous Wastes——Extraction is not presently widely used as a recovery process; however, with the development of more efficient extraction solvents (i.e., higher extraction coefficients, lower water solubility) combined with the higher cost of organic chemicals and more stringent wastewater discharge requirements, the use of extraction for the recovery of organics even when present in very low concentrations in aqueous wastes is receiving wider attention.

b. Liquid Wastes——Not generally applicable.

c. Solid Wastes——Not generally applicable.

6. Emulsion Breaking

a. Aqueous Wastes——Significant concentrations of VOC in aqueous wastes are frequently caused by the formation of water-organic emulsions, which makes phase separation difficult. Specific emulsion breaking or separating methods such as centrifugation, flotation, filtration/coalescence separation, and chemical treatment can frequently be used for the recovery of organics occurring as emulsions, resulting in lower VOC concentrations entering terminal treatment and correspondingly lower secondary emissions.

b. Liquid Wastes——See Sect. V-C-6-a.

c. Solid Wastes——Not applicable.

7. Membrane Separations

a. Aqueous Wastes——Although not presently widely used, membrane separation techniques, such as reverse osmosis, ultrafiltration, and electrodialysis, are receiving considerable attention as potential methods for the recovery of chemicals primarily from aqueous wastes containing high concentrations of dissolved inorganic compounds (e.g., brines). The chief advantage of these techniques is their ability to treat wastes that are not normally amenable to treatment by the more common methods.

b. Liquid Wastes——Not generally applicable.

c. Solid Wastes——Not applicable.

D. ALTERNATIVE TERMINAL TREATMENT

1. Introduction

Secondary emissions can frequently be reduced by using alternative treatment or disposal methods. The bulk of current secondary emissions result from the vaporization of VOC from aqueous wastes, occurring primarily during biological treatment and pretreatment operations conducted in open-topped vessels or basins. Because most processes in the SOCMI discharge extremely large quantities of wastewater, the terminal treatment and disposal methods discussed below are seldom practical as alternatives to biological treatment for the total wastewater effluent. However, specific aqueous wastes that contain relatively high concentrations of VOC or that are not readily amenable to biological treatment frequently can be separated and treated by other methods to reduce secondary emissions.

Table V-3. Current Applications of Incineration to the Disposal of Liquid and Solid Wastes

Product/Process	Company	Location	Type of Waste
Acetic acid	Borden	Geismer, LA	Distillation heavy ends
	Monsanto	Texas City, TX	Distillation heavy ends
	Celanese	Clear Lake, TX	Distillation bottoms
	Union Carbide	Brownsville, TX	Distillation light and heavy ends
Acetic anhydride	Tennessee Eastman	Kingsport, TN	Distillation light ends
	Celanese	Pampa, TX	Still residue (solid)
Acrolein	Union Carbide	Taft, LA	Distillation light ends
Acrylic acid/esters	Union Carbide	Taft, LA	Polymeric residues
	Rohm and Haas	Deer Park, TX	Heavy ends
	Celanese Chemicals Co.	Clear Lake, TX	Organic liquids; polymeric residues
Adipic acid	Du Pont	Orange, TX	Waste oil stream
Aniline	Du Pont	Beaumont, TX	Aniline tars
Butadiene	Petro-Tex	Houston, TX	Furfural purification residue
Caprolactam	Dow Badische	Freeport, TX	Extraction-tower bottoms; benzene extraction raffinate
CC/4/perchloroethylene (clorinolysis)	Dow Chemical	Plaquemine, LA	Waste chlorocarbons; solids wastes
	Vulcan	Geismar, LA	Distillation heavy ends
	Vulcan	Wichita, KA	Distillation heavy ends
Chloroprene	Denka	Houston, TX	Dehydrochlorination residue (incinerated off-site)

Table V-3. Cont'd

Product/Process	Company	Location	Type of Waste
oroprene	Du Pont	La Place, LA	Organic layer from wastewater; solid polymeric waste
ene	Monsanto	Alvin, TX	Distillation bottoms
lohexanol/ yclohexanone	Union Carbide	Taft, LA	Light and heavy ends
	Dow Badische	Freeport, TX	Light and heavy ends
yl acetate	Tennessee Eastman	Kingsport, TN	Reactor sludge
ylene dichloride	PPG Industries	Lake Charles, LA	Chlorinated residues
	Dow Chemical	Oyster Creek, TX	Chlorinated residues
	Conoco	Westlake, LA	Distillation heavy ends
	Borden	Geismar, LA	Chlorinated residues
	Shell	Deer Park, TX	Distillation light and heavy ends
amethylenediamine	Du Pont	Victoria, TX	Clorinated organics
	Monsanto	Decatur, AL	Light and heavy ends
ear alkylbenzene	Union Carbide	Institute, WV	Residual tars
aic anhydride	Amoco	Chicago, IL	Distillation bottoms
hanol	Rohm and Haas	Deer Park, TX	Purification waste liquid
	Celanese	Bishop, TN	Distillation light ends
	Air Products	Pensacola, FL	Distillation
	Tenneco	Houston, TX	Extraction and refining
hyl ethyl ketone	Arco Chemical Co.	Channelview, TX	Organic polymers
hyl methacrylate	Rohm and Haas	Deer Park, TX	Light ends
	Du Pont	Memphis, TN	Spent acid (10% VOC); polymeric residue
loroethylene	Dow Chemical	Freeport, TX	Chlorinated tar

Table V-3. Cont'd

Product/Process	Company	Location	Type of Waste
Perchloroethylene	Diamond Shamrock	Deer Park, TX	Chlorinated organics and tars
Perchloroethylene/ trichloroethylene	PPG Industries	Lake Charles, LA	Distillation residues
Phenol acetone	Georgia Pacific	Plaquemine, LA	Light and heavy oils
1,1,1-Trichloroethane	Vulcan	Geismar, LA	Chlorinated residues
Vinyl acetate	Celanese	Bay City, TN	Heavy ends from acetic acid purification
	Union Carbide	Texas City, TX	Polymeric residues
	Celanese	Clear Lake, TX	Heavy ends
	U.S.I. Chemicals	Deer Park, TX	Acid purification; heavy ends
	Du Pont	La Porte, TX	Distillation light ends; tars

2. Incineration

a. General——Secondary emissions resulting from the incineration of wastes are usually relatively low compared to alternative terminal disposal methods, and incineration is frequently the primary alternative disposal method to be considered as a means of reducing secondary emissions. Incineration is used for the disposal of liquid and solid wastes containing relatively high concentrations of organic compounds. Table V-3 presents some specific examples in which incineration is used for the terminal disposal of liquid and solid wastes.

b. Aqueous Wastes——Because of the high fuel usage necessary, incineration is usually restricted to relatively small quantities of aqueous wastes (see Sect. V-D-2-a).

c. Liquid Wastes——Although incineration is generally a versatile method, wastes containing significant concentrations of certain inorganic compounds (e.g., heavy metals, halogens, low-melting salts, phosphorous) may not be readily amenable to incineration.

d. Solid Wastes——See Sect. V-D-2-c.

3. Deep-Well Disposal

a. Aqueous Wastes——Secondary emissions resulting from deep-well disposal are generally low. Significant emissions may result from the storage of wastes (e.g., open basins, lagoons) prior to deep-well injection. Because the availability and capacity of deep-well storage are generally limited, its use is usually restricted to aqueous wastes that are not amenable to biological treatment (e.g., brines).

b. Liquid Wastes——Deep-well disposal is usually restricted to liquid wastes that are not amenable to disposal by incineration.

c. Solid Wastes——Not generally applicable except for solids in solution.

4. Landfill

a. Aqueous Wastes——Landfilling is not generally used for the disposal of large quantities of aqueous wastes. Landfilling may be used for the disposal of relatively small quantities of aqueous wastes that are not amenable to biological treatment.

b. Liquid Wastes——Since landfilling can result in significant secondary emissions, it is not generally considered as a likely alternative for secondary emission reduction; however, if the wastes are stabilized before being landfilled (see Sect. V-E-5), secondary emissions are generally minimal.

c. Solid Wastes——The disposal alternatives for solid wastes are generally limited to either landfilling or incineration. If the solid wastes contain significant concentrations of VOC, the secondary emissions are usually less from incineration than from landfilling.

5. Advanced Biological Treatment Methods

a. Aqueous Wastes——Secondary emissions from some of the more recently developed biological treatment processes (e.g., enriched oxygen, fluidized bed) are probably relatively low compared with those from conventional biological treatment processes. Although no secondary emission data for these processes are available, the general use of enclosed reaction vessels probably results in lower secondary emissions than those that occur from the open-topped basins commonly used for conventional biological treatment.

b. Liquid Wastes——Not applicable.

c. Solid Wastes——Not applicable.

E. ADD-ON CONTROLS

1. Introduction

The addition of "tail-end" controls to existing terminal treatment/disposal operations probably provides the greatest potential for the reduction of current secondary emissions from the SOCMI. As the bulk of controllable secondary emissions emanate from the biological treatment and/or pretreatment of aqueous wastes and from the landfilling of liquid and solid wastes, the emphasis in this section and in Sect. VI ("Impact Analysis") is on the control of secondary emissions from these sources. Although Table V-1 shows a number of possible control options for most secondary emission sources, only those sources with significant emission potential and the most probable control options are discussed here.

2. Covers

a. Aqueous Wastes——Covers can be effectively used to reduce secondary emissions occurring during the biological treatment, the surface impoundment, and the phase separation of aqueous wastes.

Biological treatment——Most secondary emissions are caused by the evaporation from open-topped basins commonly used in biological wastewater treatment systems. Secondary emissions from open-topped basins can be effectively controlled with covers. A floating cover is being used for odor control in anaerobic lagoon wastewater treatment.[1,2] The covers are used to contain the anaerobically generated gas and to channel the gas to an odor control device, such as a flare. Floating covers could also be used to reduce secondary VOC emissions from some types of nonaerated wastewater treatment systems, such as clarifiers and neturalization basins. In aerated wastewater treatment systems with submerged aerators a floating cover can also be used to convey secondary VOC emissions to a control device, or a rigid equipment cover fabricated from steel, aluminum, or fiber-reinforced plastic could also be used although at a higher cost.[3,4] The use of covers may not be feasible for the control of emissions from aerated systems equipped with surface aerators.

Actual field experience is limited on the floating-cover concept as a secondary VOC emissions control or conveying system. An immiscible organic liquid, plastic spheres, and plastic covers are three types of floating covers in use that may be feasible for secondary VOC emission control for nonaerated basins.

Three acrylonitrile manufacturing plants in Texas use an approximately 0.1-m-thick layer of high-molecular-weight lubrication oil to reduce secondary VOC emissions from a settling basin. The settling basin is a suspended-solids removal device located ahead of the wastewater deep well.[5] The lubrication oil is periodically replaced as it is lost through solubilization and evaporation.[6] Sampling and analysis of a controlled settling basin and of an identical uncontrolled basin showed that the controlled basin had reduced the secondary VOC emissions approximately 90%. Within the estimated statistical limits of sampling accuracy, however, the VOC emission reduction for the controlled settling basin ranged from 70 to 100%.[5]

The floating, immiscible, organic liquid is probably the most economical of the three cover types; however, the organic liquid layer will evaporate and be a source of secondary VOC emissions. A plant located in Texas reports an emission factor of approximately 2.5 to 5 kg/(yr)(m^2) for the lubrication oil cover.[6]

Plastic spheres have been used to reduce emissions of hydrocarbons from fixed-roof crude-oil storage tanks in the petroleum industry. The plastic spheres are microscopically small, hollow, and filled with gas. Tests made in the United States and Canada have shown an evaporation loss reduction of 50 to 70% for working tanks and 70 to 90% for static tanks. A 1.25- to 2.5-cm-thick blanket of spheres is generally used.[7]

Larger floating plastic spheres are used to reduce the heat loss, evaporation, and odors from a sewage digester in an European wastewater plant. The spheres are 45 mm in diameter, are made of polypropylene, and have a molded-in circumferential rim. The rim causes the spheres to interlock and reduces the problem of rotating balls exposing a film of wastewater to the atmosphere. The spheres come in diameters of 20, 45, and 150 mm. Tests showed that a single-layer blanket of 45-mm-diam spheres reduced heat losses by 70%, evaporation losses by 90%, and odor by 98%.[8]

Floating plastic spheres are also used for VOC emission control in the SOCMI. For example, they are used on an API separator in a Texas ethylbenzene plant to reduce VOC emissions.[9]

A floating, plastic, gas-tight cover has been used primarily for odor control, methane collection, algae control, evaporation control, dilution control, and potable-water protection.[10] One potential technical difficulty with this concept for secondary VOC emission control is that an adhesive must be found that will allow repairs of the floating cover and withstand the corrosive action of the chemicals present in wastewaters from the SOCMI.[11] Another concern is the generation of pockets of flammable and explosive vapor mixtures under the cover, although this has not been a problem with floating plastic covers used to collect anaerobically generated methane gas.[11] The largest floating plastic covers presently installed are about 37,000 m^2 in area.

Surface impoundment——Since no data were found in the literature review on the control of secondary VOC emissions from surface impoundments, the floating plastic cover concept discussed in Sect. V-E-2-a will be considered as the control technology. While used primarily for odor control, methane collection, algae control, evaporation control, dilution control, and potable-water protection,[10] the floating plastic cover appears to be a feasible alternative for control of secondary VOC emissions from surface impoundments.

Liquid-liquid phase separation——See Sect. V-E-2-b.

b. Liquid Wastes——Covers can also be effectively used to reduce secondary emissions occurring in surface impoundment and landfilling of liquid waste and in liquid-liquid phase separations.

Surface impoundment——See Sect. V-E-2-a.

Landfill——The volatilization rate of organic liquids and solids from a landfill soil cover can be greatly reduced by increasing the compaction and water content of the soil cover.[12] In general secondary VOC emissions from properly operated landfills with adequate soil cover will be low. For special situations with particularly hazardous organic liquids or solids in a landfill, secondary VOC emissions can probably be further reduced by use of an artificial cover such as polyurethane foam over the landfill cell.[13] The type of cover material will depend on the corrosive nature of the material being landfilled. In general plastic and asphaltic materials can be applied.

Liquid-liquid phase separation——Secondary emissions from open-topped phase separators (e.g., API separators) may also be controlled with floating covers (see Sect. V-E-2-a).

c. Solid Wastes——The use of covers to reduce secondary emissions resulting from the treatment or disposal of solid wastes is limited primarily to landfill operations.

Landfill——See Sect. V-E-2-b.

3. Carbon Adsorption

a. Aqueous Wastes——Carbon adsorption can be effectively used to reduce secondary emissions resulting from the following aqueous waste treatment operations.

Biological treatment/pretreatment——Carbon adsorption has been used to control odors from municipal wastewater treatment equipment such as clarifiers, sludge thickeners, and trickling filters. The wastewater equipment is covered and vented to the carbon adsorption system.[14] The use of carbon adsorption equipment to reduce nonodorous secondary VOC emissions from wastewater treatment systems in the SOCMI is not common practice. Also, the potential for a flammable and explosive vapor mixture being generated during the handling of secondary VOC emissions is a significant design consideration.

Surface impoundment——The comments on the use of carbon adsorption to control secondary emission from biological treatment operations (Sect. V-E-3-a) also apply to surface impoundment.

b. Liquid Wastes——Carbon adsorption can be effectively used to control secondary emissions resulting from the following liquid waste treatment/storage operations.

Surface impoundment——See Sect. V-E-3-a.

Liquid-liquid phase separation——See Sect. V-E-3-a.

4. Thermal Destruction

a. Aqueous Wastes——Although thermal destruction is not generally used for the direct disposal of aqueous wastes, it can be effectively used to control secondary emissions from other aqueous treatment/disposal operations.

Biological treatment/pretreatment——The two thermal destruction control options discussed below are a fume incinerator and a nearby fire box to reduce secondary VOC emissions from a wastewater treatment system.

Fume incinerators, both thermal and catalytic, have been used to reduce odor from both municipal and industrial wastewater systems. A recent thermal installation, for example, collects off-gas from two covered biological aeration lagoons. The unit is designed to handle approximately 1700 m^3 of off-gas per hour and recovers energy as steam.[15] A pharmaceutical plant also thermally oxidizes the odors from its wastewater treatment plant.[16] The use of fume incineration to reduce nonodorous secondary VOC emissons from wastewater treatment systems in the SOCMI is not common practice. Moreover, the potential for a flammable and explosive vapor mixture being generated during the handling of secondary VOC emissions is a significant design consideration.

A pharmaceutical plant uses a steam boiler fire box to thermally oxidize foul odors from its fermentation systems.[16] The cost-effective use of this control technology is dependent mainly on the following factors: the distance of the source of the secondary VOC emissions from the fire box, the combustion air requirement of the fire box relative to the amount of foul air, the oxygen content of the collected secondary VOC emissions, and the chemical composition of the secondary VOC emissions. VOC emissions containing organic halogens, sulfur, phosphorous, and nitro compounds could result in unacceptable boiler corrosion or stack emissions of hydrogen halide, sulfur dioxide, phosphorous pentoxide, or nitrogen oxides. Generation of flammable and explosive gas mixtures during handling is also a potential hazard for this control technology.

Surface impoundment——The comments on the use of thermal destruction for the control of secondary emissions from biological treatment operations (Sect. V-E-4-a) also apply to surface impoundment.

Liquid-liquid phase separation——See Sect. V-E-4-a.

b. Liquid Wastes——Thermal destruction can also be used for the control of secondary emissions resulting from the following liquid waste treatment and storage operations.

Surface impoundment——See Sect. V-E-4-a.

Liquid-liquid phase separation——See Sect. V-E-4-a.

c. Solid Wastes——Probably not applicable.

5. Stabilization

a. Introduction——Stabilization is the term used for any process that converts a liquid or solid waste into a chemical or physical form that will prevent or limit the release of hazardous material to the environment. Although stabilization is most often used to prevent the release of chemicals from landfill sites into natural waters, it is probably concurrently effective in controlling secondary emissions. No data are currently available on application or effectiveness.

b. Aqueous Wastes——Not generally applicable.

c. Liquid Wastes. Landfill——See Sect. V-E-5-a.

d. Solid Wastes. Landfill——See Sect. V-E-5-a.

6. Refrigerated Condensers

a. General——Refrigerated condensers are commonly used in the SOCMI to control emissions from process storage tanks containing VOC.[17] Although specific examples in which refrigerated condensers have been used for the control of secondary emissions are not available, condensers would probably be suitable for applications in which the concentration of VOC in emitted vapor is relatively high. The VOC removal efficiency of a refrigerated condenser is primarily dependent on the condenser temperature, the concentration of VOC in noncondensable gases vented (i.e., air, nitrogen), and the vapor pressure of the contained VOC.

b. Aqueous Wastes——Applications of the refrigerated condensers to the control of secondary emissions from aqueous waste treatment are discussed below.

Biological treatment/pretreatment——Application would be limited to the control of secondary emissions from non-aerated basins (e.g., clarifiers, thickeners, neutralization basins) and would require the basins to be covered and vented to the refrigerated condenser.

Surface impoundment——See Sect. V-E-6-b.

Liquid-liquid phase separation——See Sect. V-E-6-b.

c. Liquid Wastes——Since the concentration of organics in the secondary emissions occurring with the following liquid waste treatment or storage operations is frequently greater, the use of refrigerated condensers may be more suitable than for corresponding aqueous waste treatment applications.

Surface impoundment——See Sect. V-E-6-b.

Liquid-liquid phase separation——See Sect. V-E-6-b.

d. Solid Wastes——Not applicable.

F. POTENTIAL SECONDARY VOC EMISSION REDUCTION

Table V-2 summarizes the range of estimated secondary VOC emission reduction through the use of the more significant control options discussed in this section.

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VI. IMPACT ANALYSIS

A. INTRODUCTION

The impact analysis of secondary emissions is based on a model chemical production plant (MCPP) with a model wastewater treatment system, landfill, and surface impoundment; the model parameters for these units are summarized in Tables IV-2, IV-3, and IV-5 and E-1 in Appendix E. The MCPP can be considered to be a large chemical complex producing 1650 Gg of chemicals per year with a production based on the average production of the 30 chemicals shown in Table IV-4. For simplifying purposes the organically contaminated wastewater was treated as a wastewater containing a single-component waste chemical with a Henry's-law constant (M_{xi}) of 25 and a molecular weight of 58. The other wastewater parameters (shown in Table IV-3) are production-weighted averages for the 30 chemicals based on available wastewater data.[1—4]

The impact analyses for the landfill and surface impoundment are based on two model solid chemicals selected for widely varying secondary VOC emission potential. Chemical A, similar in physicochemical properties to hexachlorobenzene, has a low vapor pressure (0.0025 pascal) and chemical B, similar in physicochemical properties to dichlorobenzene, has a high vapor pressure (130 pascals). The impact analyses for landfill and surface impoundment were done separately for each chemical.

Uncontrolled secondary VOC emissions for the model wastewater treatment plant are shown in Fig. IV-1. Uncontrolled emissions of 1.06 Gg/yr are based on the industry secondary emissions factor of 640 g of VOC per Mg of product multiplied by the model-plant production of 1650 Gg/yr. The emissions shown in Fig. IV-1 from the clarifier and conventional activated-sludge (CAS) system were estimated by the methods described in Appendix B.

For the impact analysis the following options were evaluated for the control of secondary VOC emissions from the model-plant wastewater: a carbon adsorption system for recovery of the VOC from the wastewater, a cover to reduce secondary VOC emissions from the wastewater clarifier, a cover for the clarifier plus a carbon adsorption system, and a cover for the clarifier plus a CAS system using a fume incinerator. The control options are shown in Figs. VI-1—VI-4.

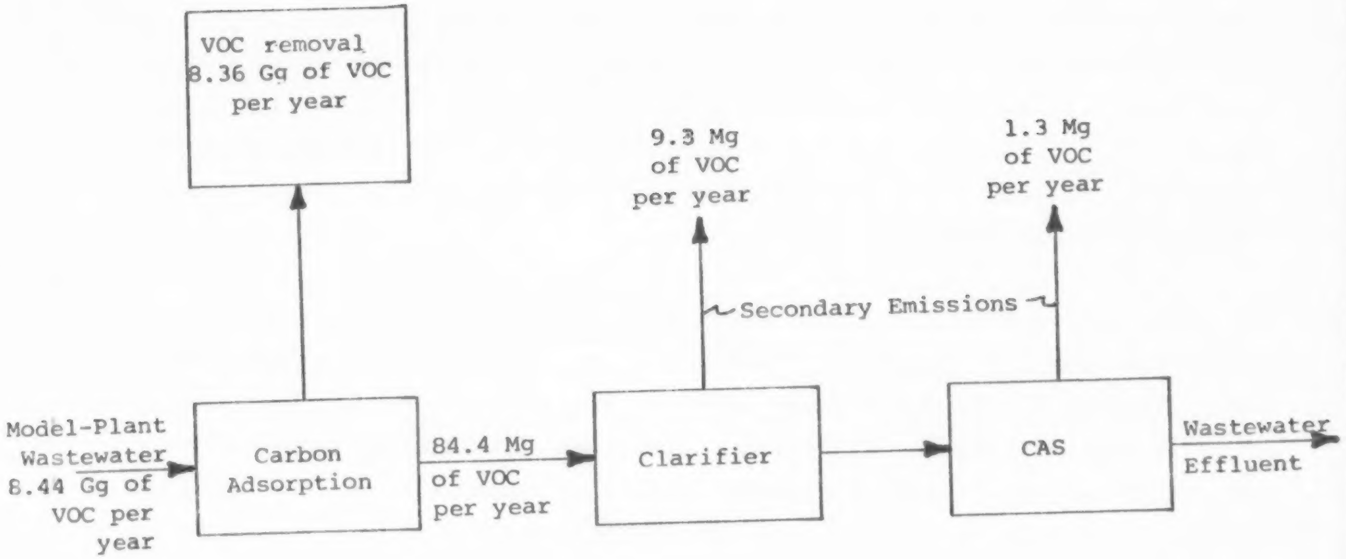

Fig. VI-1. Control Option 1: Removal of Model-Plant Wastewater VOC with Carbon Adsorption (Total, 10.6 Mg of VOC Emissions Per Year)

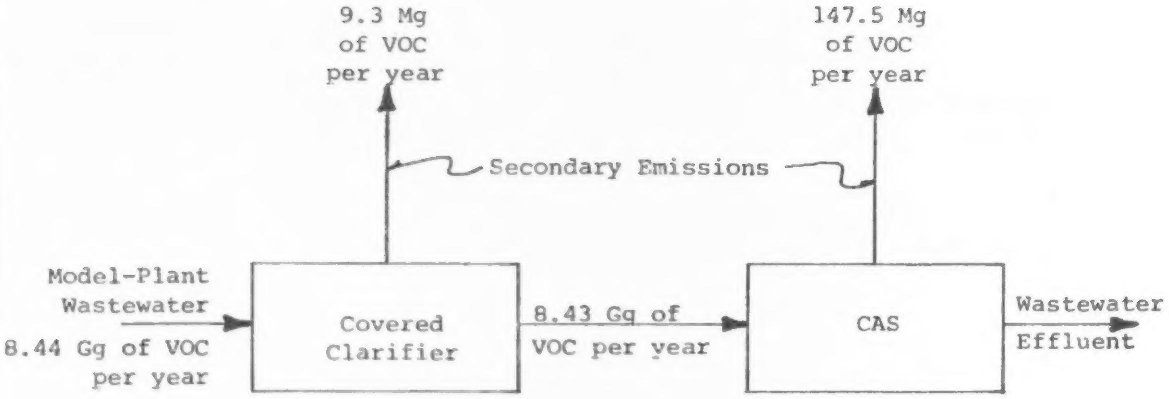

Fig. VI-2. Control Option 2: Cover for Model-Plant Wastewater Clarifier
(Total, 157 Mg of VOC Emissions Per Year)

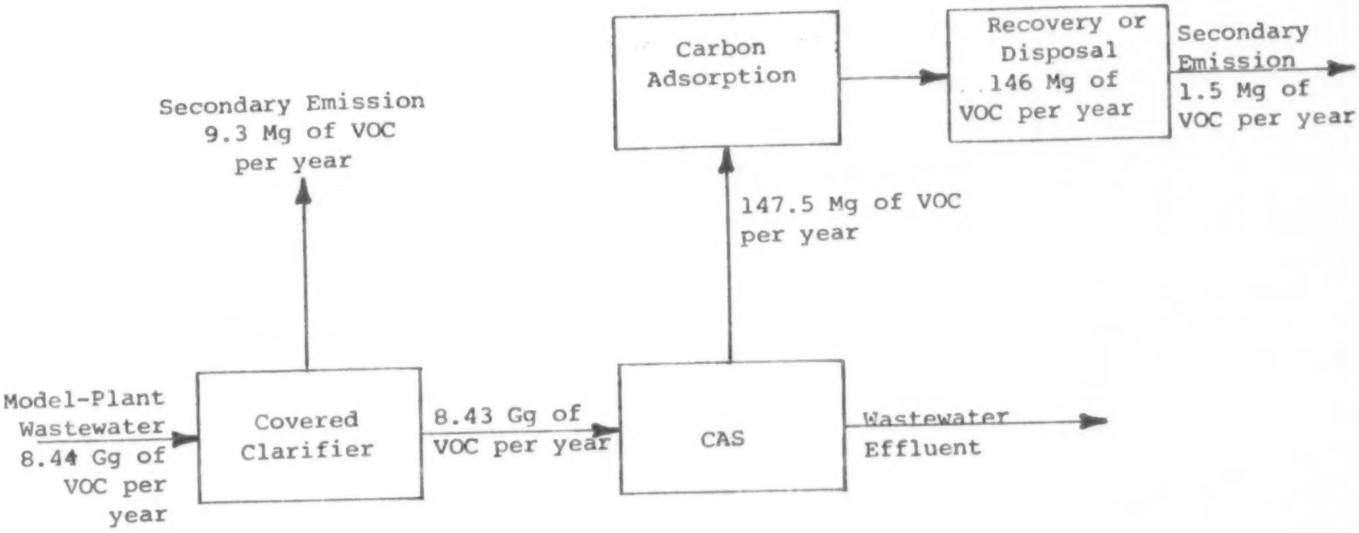

Fig. VI-3. Control Option 3: Covered Clarifier Plus Carbon Adsorption (With and Without Chemical Recovery) of the Secondary VOC Emissions from a CAS System Treating the Model-Plant Wastewater (Total, 10.8 Mg of VOC Emissions Per Year)

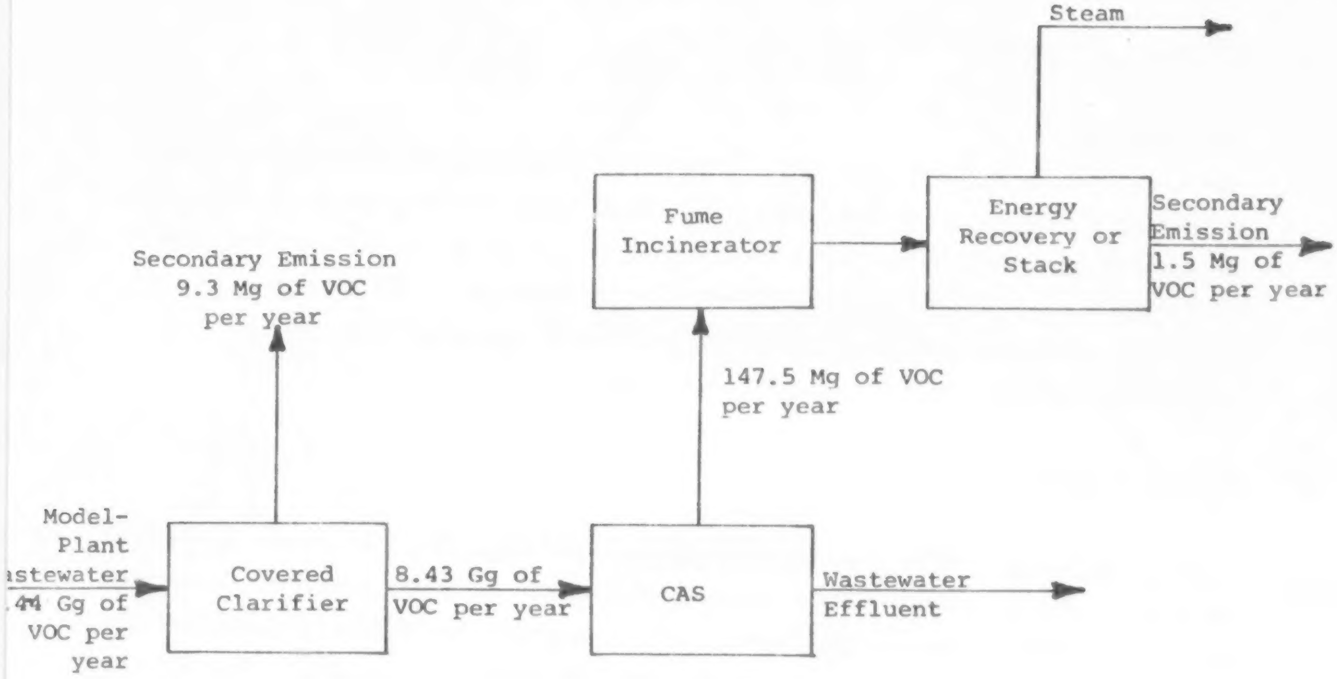

Fig. VI-4. Control Option 4: Covered Clarifier Plus Fume Incineration (With and Without Energy Recovery) of the Secondary VOC Emissions from a CAS System Treating the Model-Plant Wastewater (Total, 10.8 Mg of VOC Emissions Per Year)

The impact analysis for the liquid and solid organic wastes is based on the model-plant parameters summarized in Table IV-5 and Table E-3 in Appendix E. The reduction of secondary VOC emissions from an existing landfill and surface impoundment by means of gas-tight plastic covers is evaluated.

B. CONTROL COST IMPACT

1. Introduction

The estimated costs and cost-effectiveness data for control of secondary VOC emissions resulting from the model-plant production are presented in Table VI-1. Details of the model chemical production plant are given in Tables IV-2, IV-3, IV-5, and E-3; cost estimate calculations are included in Appendix E. The following model-plant analyses are for estimation purposes only and not for standards support.

2. Aqueous Wastes

a. Control Option 1——With this control option (see Fig. VI-1) a carbon adsorption system is used to remove 99% or greater of the VOC from the model-plant wastewater. In some instances the removal efficiency will be slightly decreased by VOC losses during regeneration or subsequent decanting operations. The VOC in the carbon adsorption system wastewater effluent then enters the model-plant wastewater treatment system described in Table IV-2. Recovery of the VOC from the wastewater before it enters the model wastewater treatment plant results in a 99% reduction of secondary VOC emissions relative to the uncontrolled base case shown in Fig. IV-1. The bases for control option 1 are given in Sect. A-1 of Appendix E.

The estimated capital cost of a carbon adsorption system designed to reduce by 99% or greater the model-plant wastewater is $3,900,000 (see Table VI-1). This cost is based on the installation of a carbon adsorption system consisting of skid-mounted beds, blowers, condensers, decanter, interconnecting piping, valving, instrumentation, and all necessary piping and utility connections.

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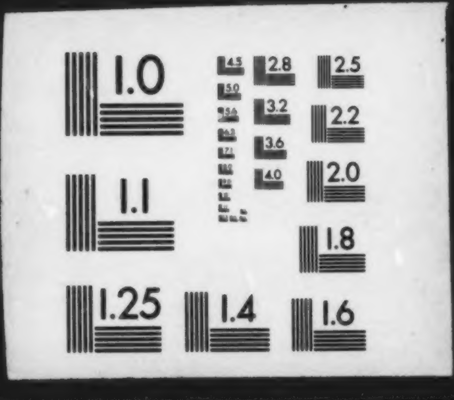

Table VI-1. Cost Estimates for Control of Secondary VOC Emissions for Model Plant

		Annual Operating Cost, December 1979						Emission Reduction		
Cost Item	Total Installed Capital Cost	Utilities and Raw Materials	Manpower	Capital Related Costs	Contract Waste Disposal Costs	Recovery (Credits)[a]	Net Annual Costs	(Mg/yr)	(%)	Effectiveness[b] (per Mg)
Wastewater										
Carbon adsorption (CA)[c]	$3,900,000	647,000	39,400	1,131,000			$1,817,400	1049	99	$ 1,733
Cover for clarifier[d]	75,320						21,840	903	85	24
Cover and CA with chemical recovery[e]	1,363,200	25,700	39,400	21,840		(26,300)	434,100	1049	99	414
Cover and CA without chemical recovery[c]	1,363,200	25,700	39,400	395,300	$17,500		477,900	1049	99	456
Cover and fume incineration (FI) without energy recovery[f]	1,583,200	909,300	27,000	459,100			1,395,400	1049	99	1,330
Cover and FI with energy recovery[f]	2,153,200	910,100	27,000	624,400		(598,700)	962,800	1049	99	918
Landfill										
Cover/chemical A[g]	435,600			126,300			126,300	3×10^{-4}	99	420,000,000
Cover/chemical B[h]	435,600			126,300			126,300	12	99	10,500
Surface impoundment										
Cover/chemical A[g]	435,600			126,300			126,300	0.014	99	9,000,000
Cover/chemical B[h]	435,600			126,300			126,300	274	99	460

[a] Net annual cost and cost effectiveness depend strongly on recovery credits.

[b] Cost per Mg of VOC emission reduction.

[c] See Fig. VI-1.

[d] See Fig. VI-2.

[e] See Fig. VI-3.

[f] See Fig. VI-4.

[g] Low-vapor-pressure solid.

[h] High-vapor-pressure solid.

To determine the cost effectiveness of the carbon adsorption system, estimates were made of the direct operating cost, the capital recovery cost, and the miscellaneous capital costs. Three cases were evaluated using recovery credits of 0, \$0.18, and \$0.36 per kg of recovered VOC. For control option 1 the net annual cost is \$1,817,000 based on a zero recovery credit. The cost effectiveness for this control option is \$1733 per Mg of VOC reduction.

The net annual cost and the cost effectiveness for this control option are directly proportional to the VOC recovery credit. For a VOC recovery credit of \$0.18 per kg of VOC the net annual cost is \$312,400 and the cost effectiveness is \$298 per Mg of VOC reduction. For a \$0.36 per kg of VOC recovery credit the net annual savings would be \$1,137,000 and the cost effectiveness would be a savings of \$1,137 per Mg of VOC reduction. The cost effectiveness for this control option is also strongly dependent on the quality of the recovered VOC. Additional unit operations such as distillation to upgrade the recovered VOC will result in higher net annual costs than those given.

b. Control Option 2——With this control option (see Fig. VI-2) a floating gas-tight plastic cover on the model-plant wastewater clarifier, 99% or greater of the uncontrolled secondary VOC emissions from the clarifier are reduced. This means that more VOC is treated in the CAS unit, which slightly increases the secondary emissions from the CAS unit. The secondary VOC emissions from the CAS system are uncontrolled in this option. Covering the clarifier results in an 85% reduction of secondary VOC emissions relative to the uncontrolled base case shown in Fig. III-1.

The estimated installed capital cost of such a cover designed to reduce by 99% or greater the clarifier secondary VOC emissions is \$75,320 (see Table VI-1). To determine the cost effectiveness of this control option, estimates were made of the capital-related costs (see Appendix E). For this control option the annual cost is \$21,840. The cost effectiveness for the control option is \$24 per Mg of VOC emission reduction for the model chemical having an M_{xi} of 25.

c. Control Option 3——This control option (shown in Fig. VI-3) consists of carbon adsorption (with and without chemical recovery) of the secondary VOC emissions from a CAS system treating the model-plant wastewater. The clarifier and CAS system are covered with a gas-tight cover, and the off-gas VOC emissions from the CAS are removed by a carbon adsorption system. The VOC removal efficiency of the carbon adsorption system is 99% or greater. The clarifier cover and the carbon adsorption system result in a 99% reduction of secondary VOC emissions relative to the uncontrolled base case shown in Fig. III-1.

The estimated capital cost of a carbon adsorption[5] and cover system (floating plastic cover) designed to reduce by 99% or greater the model-plant wastewater VOC is $1,360,000 (see Table VI-1).

To determine the cost effectiveness of the covers and carbon adsorption system, estimates were made of the direct operating cost, the capital related cost, and the miscellaneous capital costs. For this control option without chemical recovery, the net annual cost, including disposal charges, is $478,000. The net annual cost for the option with chemical recovery is directly proportional to the value of the recovered chemical and ranges from $460,500 to $407,900 for recovery credits ranging from zero to $0.36 per kg of recovered VOC.

The cost effectiveness for the option with chemical recovery and a recovery credit of $0.18 per kg is $414 per Mg of VOC emission reduction. Without chemical recovery the cost effectiveness is $456 per Mg of VOC emission reduction.

For the option without chemical recovery the incremental cost effectiveness for the additional 146 Mg of VOC emission reduction resulting from the addition of the CAS cover and carbon adsorption system to the covered clarifier of control option 2 is $3124 per Mg of VOC emission reduction. For the option with chemical recovery at $0.18 per kg of recovered chemical, the incremental cost effectiveness for control option 3 over control option 2 is $2824 per Mg of emission reduction.

d. Control Option 4——This control option (shown in Fig. VI-4) consists of a covered clarifier, a covered CAS system, and a fume incineration system (with and without energy recovery) for the secondary VOC emissions from a CAS system treating the model-plant wastewater. The clarifier is covered with a floating gas-tight cover as in option 2, and the off-gas VOC emissions from the CAS system are removed by the fume incineration system. The VOC removal efficiency of the fume incineration system is 99% or greater. The clarifier cover and the fume incineration system result in a 99% reduction of secondary VOC emissions relative to the uncontrolled base case shown in Fig. III-1.

The estimated capital cost of a fume incineration[6] and cover system designed to reduce by 99% or greater the model-plant wastewater VOC secondary emissions is $1,583,200 (see Table VI-1). If waste-heat recovery is included to reduce the operating cost, the estimated installed capital cost is $2,153,200. These costs are based on a thermal oxidizer designed for a residence time of 0.5 sec at 871°C, completely installed, and include a blower, all controls and instrumentation, a complete energy recovery steam boiler, and a stack.

To determine the cost effectiveness of a thermal oxidizer, estimates were made of the direct operating cost, the capital-related cost, and the miscellaneous capital costs, both with and without heat recovery. The recovery credit was calculated for the heat-recovery case based on a boiler outlet temperature of 260°C, or the recovery of approximately 60% of the energy in the flue gases. The value of the recovered energy is credited as the cost of natural gas at $1.90 per GJ. The net annual cost without energy recovery is $1,395,400 and with energy recovery is $962,800 (see Table VI-1). The cost effectiveness without energy recovery is $1330 per Mg of VOC emission reduction and with energy recovery is $918 per Mg of VOC emission reduction (see Table VI-1).

The incremental cost effectiveness for control option 4 over control option 2 (covered clarifier) is $6440 per Mg of emission reduction with energy recovery and is $9408 per Mg of emission reduction without energy recovery.

2. Liquid Wastes

a. Landfill Plastic Cover——In this control option the model-plant landfill parameters listed in Table IV-5 were used as the basis for the estimation. Two cases are evaluated, one for model chemical A, a low-vapor-pressure solid, and the other for model chemical B, a relatively high-vapor-pressure solid. The secondary VOC emission estimates are based on the estimation methods described in Appendix D. The plastic cover is installed after a landfill cell is completed and is designed to reduce the secondary VOC emissions by 99% or greater, relative to the uncontrolled emission case.

The estimated capital cost of a plastic cover to reduce the landfill secondary VOC emissions is $435,600 (see Table VI-1). To determine the cost effectiveness of this control option, estimates were made of the capital recovery cost and the cover maintenance and miscellaneous costs (see Appendix E). For the model plant the annual cost is $126,300 each for chemicals A and B. The cost effectiveness for the model plant is $420,000,000 per Mg of VOC emission reduction for chemical A and is $10,500 per Mg for VOC emission reduction for chemical B.

Surface Impoundment Cover——In this control option the model-plant impoundment surface parameters used as the basis for the estimation are those given in Table E-1 in Appendix E. Two cases are evaluated, one for model chemical A, a low-vapor-pressure solid, and the other for model chemical B, a relatively high vapor-pressure solid. The secondary VOC emission estimates are based on the estimation methods described in Appendix C. The plastic cover is installed after the surface impoundment is filled and is designed to reduce the secondary VOC emissions by 99% or greater, relative to the uncontrolled-emission case.

The estimated capital cost of a plastic cover to reduce the surface-impoundment secondary VOC emissions is $435,600 (see Table VI-1). To determine the cost effectiveness of this control option, estimates were made of the capital recovery cost and the cover maintenance and miscellaneous costs (see Appendix E). For the model plant the annual cost is $126,300 each for chemicals A and B. The cost effectiveness for the model plant is $9,000,000 per Mg of VOC emission reduction for chemical A and is $460 per Mg of VOC emission reduction for chemical B.

Solid Wastes

Landfill Plastic Cover——See Sect. IV-B-2-a.

ENVIRONMENTAL AND ENERGY IMPACTS

Table VI-2 gives the environmental and energy impacts of reducing the secondary VOC emissions by application of the indicated control options to the model plant. Secondary VOC emissions are shown to be reduced by as much as 903 Mg/yr to 1049 Mg/yr for the model-plant wastewater and by 3×10^{-4} Mg/yr to 274 Mg/yr for the model-plant liquid and solid organic wastes. The net energy usage for the control options ranges from zero to 479 TJ per year as natural gas.

Table VI-2. Environmental and Energy Impacts of Controlled Secondary VOC Emissions from Model Plant

Emission Source	Control Option	Emission Reduction (%)	Emission Reduction (Mg/yr)	Energy Usage (TJ/yr)
Model wastewater treatment plant	Carbon adsorption (CA)[a]	99	1049	196 as steam
	Cover for clarifier[b]	85	903	
	Cover and CA with and without chemical recovery[c]	99	1049	7 as steam[d]
	Cover and fume incineration (FI) without energy recovery[e]	99	1049	479 as natural gas
	Cover and FI with energy recovery[e]	99	1049	479 as natural gas usage; 316 as recovered steam[f]
Sanitary landfill	Cover/chemical A[g]	99	3×10^{-4}	
	Cover/chemical B[h]	99	12	
Surface impoundment	Cover/chemical A[g]	99	0.01	
	Cover/chemical B[h]	99	274	

[a] See Fig. VI-1.

[b] See Fig. VI-2.

[c] See Fig. VI-3.

[d] Does not include any energy necessary for disposal.

[e] See Fig. VI-4.

[f] Net energy usage for this control option is 163 TJ/yr.

[g] Low-vapor-pressure solid.

[h] High-vapor-pressure solid.

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VII. ASSESSMENT

A. SUMMARY

Secondary VOC emissions, defined as emissions that result from the treatment and disposal of aqueous, liquid, and solid wastes, may account for as much as 5% of the total SOCMI emissions. Most secondary emissions result from the storage, treatment, and disposal of aqueous wastes, with the balance originating mainly from chemical landfill and surface impoundment of primarily liquid and solid wastes. Based on 1976 SOCMI production[1] the order-of-magnitude uncontrolled secondary VOC emissions from aqueous wastes are estimated to be 58 Gg/yr. Most of the secondary emissions from aqueous wastes that are currently uncontrolled are caused by the evaporation of VOC from open-topped basins, which are commonly used in the handling and treatment of aqueous wastes.

The add-on control alternatives for aqueous wastes that are evaluated in Sect. VI are all based on the use of covers to minimize VOC emissions and/or to collect the emissions and route them through terminal treatment/disposal devices. The range of estimated control costs for the large model plant considered varies widely from relatively low to prohibitively expensive, depending primarily on the degree of control provided. Although the use of the various types of covers to control secondary emissions from aqueous wastes is currently not widely used by industry, it is a promising approach.

B. DATA ASSESSMENT

Because secondary emissions are very difficult to measure directly, practically no direct emission data are available.

The conclusions presented in this report are based primarily on theoretically developed, order-of-magnitude estimates of emissions. The accuracy of these estimates is dependent on the availability of information on the characteristics and quantities of aqueous, liquid, and solid wastes. This information is also very scarce, particularly information pertinent to landfilling and surface impoundment operations.

In order to attain estimates of greater accuracy it will be necessary to develop a great deal more information on the quantity and characteristics of liquid and

solid wastes sent to landfill and on surface impoundment based on actual industrial experience.

C. REFERENCE*

1. Synthetic Organic Chemicals, 1976 United States Production and Sales, United States International Trade Commission, GPO, Washington (1977).

*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

APPENDIX A

LITERATURE REVIEW

Appendix A
LITERATURE REVIEW

Although the area of secondary emissions is starting to receive a lot of research attention, the topic is not a new one. For example, in 1957 Eckenfelder *et al.*[1] presented a paper on some theoretical aspects of aerating industrial wastewaters, and in 1961, Gaudy *et al.*[2,3] started publishing a series of papers on the stripping of volatile components from conventional wastewater treatment systems. The following review highlights the literature of secondary emissions relative to wastewater, liquid organic, and solid organic wastes.

A. ORGANICALLY CONTAMINATED WASTEWATER

In collaboration with others,[2,4] Gaudy did much of the early published work on secondary emissions. In other early researches[5—7] the concentration was on the removal of chemical oxygen demand (COD) from refinery wastewaters by aeration. Gaudy *et al*. concentrated on laboratory work with volatile ketones and aldehydes, for example, acetone, butanone, and propionaldehyde, and investigated air stripping of synthetic solutions during biological oxidation[8] and without biological oxidation.[2] They also investigated the air stripping of acetone in the presence of dissolved salts and found no appreciable effect on stripping caused by the salts.[3] In a recent paper[9] Gaudy investigated the formation of strippable biodegradation products in a glucose solution and found that a maximum of 3 to 4% of the glucose COD input was converted to air-strippable COD.

Much of the recent secondary-emission literature (refs. 10—12, for example) has been concerned with the estimation of secondary emissions from organically contaminated wastewaters.

Estimation Methods

There are basically two types of wastewater secondary-emission estimation methods described in the literature: estimation methods using pure-component physicochemical properties and methods using stripping constants experimentally derived in the laboratory from actual industrial multicomponent wastewater samples.

Secondary-emission estimation methods based on the pure-component physicochemical-property approach have been developed by Mackay and Leinonen,[10] Thibodeaux,[11] and Smith and Bomberger.[12] The procedures developed in refs. 10 and 11 for the estimation of secondary VOC emissions from organically contaminated wastewaters are detailed in Appendix A.

a. Mackay Method——Mackay's estimation method is based on the two-film theory of mass transfer.[13] This method has been compared with experimental data for the evaporation of selected chlorinated hydrocarbons from dilute aqueous solutions and found to produce reasonably close results.[14] The equations in ref. 10 can be used to estimate the desorption of low-solubility contaminants from nonaerated process basins without biological oxidation and from surface impoundments.

b. Thibodeaux Method——The Thibodeaux paper[11] is basically a computer-simulation study for the desorption of oxygen-containing polar compounds from wastewater treatment systems. Most of the compounds are highly soluble in water. In his paper mass balance equations are developed for the desorption of the compounds from different wastewater treatment systems, which are summarized as a function of Henry's-law constant (M_{xi}) for the compounds.

c. Smith Method——The procedure described in ref. 12 is based on the observation that for highly volatile compounds the experimentally obtained ratio of the desorption rate constant to the oxygen reaeration rate constant is a constant for a range of turbulent conditions. In that paper an activated-sludge process is modeled, and the calculated desorption of various chemical compounds in the modeled activated-sludge process is summarized.

Secondary-emission estimation studies based on laboratory-derived stripping constants for multicomponent wastewaters have been published by Thibodeaux and Millican[15] and by Richardson and Ledbetter.[16]

d. Thibodeaux Study——In this study wastewater is pumped from the bottom of a flask back into the flask, where the liquid irrigates a section of packing. Air is forced into the flask below the packing to produce countercurrent contact in the packing and desorption of the volatile fractions of the organics in the wastewater. As many as 75 wastewater samples representing 26 industry types were tested by the stripping-constant method.

e. Richardson Study—In this study 5-liter samples of biologically inert multicomponent wastewater samples were aerated by a centrifugal air blower. Before the air supply entered the sample bottle, it was presaturated with water to minimize water evaporation. Different air flows were used in the laboratory work, and a regression equation was obtained for the stripping-rate constant as a function of stripping air flow. The industrial effluent tested consisted mainly of wastewaters from a compressed-gas plant, two petroleum refineries, a petrochemical plant, and a kraft pulp and paper mill.

2. Field Studies

There are very few published studies of full-scale industrial wastewater treatment systems that have been sampled and analyzed for secondary emissions. Most of the published studies have been done for petrochemical and petroleum refinery wastewaters. These studies are summarized below.

a. Los Angeles County Study on Petroleum Refineries[17]—In this pioneering study of petroleum refinery emissions, field inspections were made at six major refineries in Los Angeles County for secondary emissions from process drains and wastewater treatment systems. During the inspections a combustible gas indicator was used to determine the hydrocarbon vapor concentrations, and a titanium tetrachloride smoke tube was used to indicate the approximate air flows associated with the hydrocarbon concentration.

The wastewater systems inspected were drain sumps (collection basins), interceptor systems, oil-water separators, and open secondary flotation tanks or ponds. Hydrocarbon vapor concentrations were found above the surface of all these wastewater systems except the open secondary flotation tanks or ponds. Since air flows during the inspections were not quantitatively determined, secondary emissions could not be calculated. The secondary emissions estimated in the report[17] were based on a total-pollution survey by the Air Pollution Control District.[18] The secondary emissions for all six refineries were estimated to be 2.7 Mg of hydrocarbons per day, which is approximately equal to an emission factor of 2.4 kg of hydrocarbons per 1000 m^3 of wastewater.

b. German Study on Refineries and Chemical Factories[19]—In this paper the author states that the average quantities of exhaust gas exiting the wastewater ducts of refineries and chemical factories are estimated to be 12 kg per 1000 m^3 of plant wastewater throughput. No comments are made in the paper as to how this emission factor was obtained.

c. EPA Study on Acrylonitrile Manufacture[20]——In the manufacture of acrylonitrile by the catalytic vapor-phase amoxidation of propylene a settling basin is used as a solids removal device for process wastewater before it is injected into a deep well. As a VOC control device three of the manufacturing plants cover the surface of the settling basin with about 0.1 m of lubricating oil having a molecular weight of about 500. Field sampling during this study was done on both controlled and uncontrolled secondary emissions from the settling basin. Sampling was done to obtain ambient air samples upwind and downwind of the basin.

d. Richardson Study on Mixed Industrial Wastes[16]——In this work, which was discussed earlier, both laboratory and field observations were made. In the field work an inverted funnel that was floated on the surface of an aeration basin was used to minimize atmospheric dilution. The funnel conveyed the off-gas directly to a portable gas chromatograph. The aeration basin sampled was treating wastewater from many facilities, most of which were petrochemical industries. Four sampling sites were selected: at the ends and at points one-third the distance from each end of an interior bay of a six-bay aeration basin. The secondary emissions found were reported as methane.

3. On-Going EPA Work

The EPA is currently assessing secondary emissions from industrial and municipal wastewaters in the following on-going studies:

a. Oil Refinery Wastewater Systems——In this study, conducted by the Research Triangle Park, North Carolina, office, two dissolved air flotation (DAF) systems and five wastewater separators in oil refineries have been evaluated. A mass-balance method is being used for secondary-emission determination. Wastewater influent and effluent samples are analyzed for hydrocarbon concentration, and the difference is taken as the hydrocarbon secondary emission. At this time no data have been made public from the DAF and API units.

b. Robert S. Kerr Environmental Research Laboratory[22]——In this assessment by the Ada, Oaklahoma, office, priority pollutants in the wastewater treatment systems of ten plants from five different industries have been studied. As part of the study a mobile air-stripping column has been used to collect volatile organics from the mixed liquor-suspended solids in five industries. At this time no results have been made public relative to the air stripping of organics from these wastewater streams.

. Municipal Environmental Research Laboratory[23]—The Wastewater Research Division in Cincinnati has started to assess the secondary emissions of priority pollutants from publicly owned treatment works. The program, which will include laboratory and field studies of priority pollutant secondary emissions, will evaluate predictive techniques, development of techniques, and field sampling and analysis.

1. Water Quality Analysis Branch[23]—This study, which is being done by the Washington, D.C., office, will concentrate on priority pollutant identification in publicly owned treatment works and will also include field sampling and analysis of priority-pollutant secondary emissions from 40 such works.

3. LIQUID AND SOLID ORGANIC WASTES

The sampling, analysis, and characterization of secondary emissions from the treatment and disposal of liquid and solid organic wastes have not received as much attention as secondary emissions from wastewaters. Most of the secondary-emission studies found in a brief literature review were concerned with methane generation in sanitary landfills handling municipal refuse, which is outside the scope of this report. A few references were found for secondary emissions from sanitary landfills and surface impoundments, and are summarized in the following sections.

1. Estimation Methods

Secondary emissions from sanitary landfills and from surface impoundments were studied by Farmer et al.[24—26] and by Mackay[10] respectively.

The most comprehensive work to date on emissions from landfills has been done by Farmer et al. in a series of papers concerned with the land disposal of hexachlorobenzene (HCB). Using HCB waste, the authors determined in the laboratory the important soil parameters controlling HCB vapor movement out of the soil cover. Based on these research findings they developed predictive equations for use in designing landfill soil covers to reduce organic vapor movement out of a landfill.

The technique developed by Mackay[10] is the most reasonable method of estimating secondary emissions from a surface impoundment. The surface impoundment should be considered to be an organic liquid or organic solid waste covered by a layer of water. The Mackay model is a diffusion model only and does not incorporate aerobic or anaerobic degradation mechanisms.

2. Field Studies

Vinyl chloride monomer (VCM) emissions at a landfill used for polymerization sludges have been assessed by bag-sampling techniques.[27]

No information on field studies of secondary emissions from surface impoundments was found.

3. On-Going EPA Work

The Solid and Hazardous Waste Research Division of the Municipal and Environmental Research Laboratory in Cincinnati, Ohio, is funding a study to sample and measure the levels of air pollutants that might be emitted from hazardous waste management facilities located throughout the United States.[28] Among the areas tested will be landfill, chemical/biological treatment, transfer operations, and storage facilities.

Under a grant to the University of Arkansas, wastewater treatment basins at pulp and paper mills will be sampled to determine the magnitude of selected chemical air emissions. The compounds selected for study are methanol, acetone, acetaldehyde, hydrogen sulfide, methyl mercaptan, and dimethyl disulfide. A sampling method for upwind/downwind measurements of the basin is also being developed.

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APPENDIX B

ESTIMATION PROCEDURES FOR SECONDARY VOC EMISSIONS FROM WASTEWATER

Appendix B
ESTIMATION PROCEDURES FOR SECONDARY VOC EMISSIONS FROM WASTEWATER

This appendix summarizes three procedures that were obtained from the literature for estimating secondary VOC emissions from wastewater treatment systems and describes how they are used in this report: the Mackay[1] and Dilling[2] methods for nonaerated flow systems such as a clarifier; the Thibodeaux[3] method for aerated flow systems such as activated-sludge treatment; and the Mackay[1] method for nonaerated and nonflow systems such as a surface impoundment. Because of the limitations discussed later in this appendix the secondary VOC emission estimates based on the three methods should be considered to have an order-of-magnitude value.

A. HENRY'S-LAW CONSTANT (M_{xi})

Inherent in the use of the procedures to estimate the secondary VOC emissions from wastewater is the need for a Henry's-law constant for the organic contaminant. Either of two methods may be used to estimate this constant: the use of vapor-liquid equilibrium data at a temperature close to the wastewater temperature or the use of pure-component vapor pressure and solubility data for compounds that have low water solubility.

1. Estimation by Vapor-Liquid Equilibrium Data

The vapor-liquid equilibrium method for estimating M_{xi} is limited because the equilibrium data needed generally must be at ambient temperature to simulate wastewater temperatures. However, it is the best estimation method for highly water soluble compounds.

The following derivation describes how vapor-liquid equilibrium data can be used to calculate Henry's-law constant:

Since the fugacity coefficient is equal to unity for many dilute organic aqueous systems, the constant, in units of atmosphere,[3] can be expressed as

$$M_{xi} = \lim_{x_i \to 0} \left(\frac{Y_i P}{x_i} \right) , \qquad (1)$$

where

Y_i = the mole fraction of the organic compound in the vapor phase,
x_i = the mole fraction of the organic in the aqueous phase,
P = the total pressure of the system in atmospheres.

An example of the use of equilibrium data for estimating the above constant is shown below for acetone in water at 25°C:

x_i	Y_i	P (mm Hg)
0.01936	0.5234	50.1
0.0289	0.6212	61.8
0.04495	0.7168	81.3

At $x_i = 0.01936$

$$\frac{Y_i P}{x_i} = \frac{(0.5234)(50.1)}{0.01936} \frac{1}{760}$$

$$= 1.782.$$

M_{xi} is then developed from a plot of x_i versus $Y_i P/x_i$. The intercept of $Y_i P/x_i$ for x_i equal to zero is Henry's-law constant. In this case the intercept of $Y_i P/x_i$ at x_i equal to zero, using nonlinear curve fitting, is about 2. This value should then be corrected from 23.7 mm Hg, the saturation pressure of the water at 25°C, to 760 mm. This correction is small and in light of the order-of-magnitude type of analysis being performed can be ignored.

2. Estimation by Solubility Data

For compounds with low water solubility (about 10% or less by weight) M_{xi} can be estimated from the saturated solubility of the compound in water and the vapor pressure of the pure compound, both at the temperature of the system.

For a saturated solution it is assumed that $x_i = x_{is}$ and that the partial pressure of the compound in solution, $\bar{P}_i$, is the same as the vapor pressure, P^*_{ia}, of the pure compound. This will be true for systems in which the water is relatively insoluble in the compound and fugacity coefficient, Φ, is equal to 1. This can be expressed as

$$M_{xi} = \frac{Y_i P}{x_i} = \frac{\bar{P}_i}{x_i} = \frac{P^*_{ia}}{x_{is}} \quad , \qquad (2)$$

where

P^*_{ia} = the pure-component vapor pressure of the compound at the temperature of the system in atmospheres,

x_{is} = the mole fraction at saturated solubility of the compound in the water at the temperature of the system,

M_{xi} = Henry's-law constant in atmospheres.

Since most solubility data are given in mg/liter or in ppm and most vapor pressure data in mm Hg, Eq. (2) can be rewritten as the following approximate equation (valid when Si < 100,000 mg/liter) by applying conversion factors for the units involved:

$$M_{xi} = \frac{P^*_i M_{wi}(10^6)}{S_i(18)(760)} = \frac{73\ P^*_i M_{wi}}{S_i} \quad , \qquad (3)$$

where

P^*_i = the pure-component vapor pressure of the compound at the temperature of the system, in mm Hg,

M_{wi} = the molecular weight of the compound,

S_i = the saturated solubility (in mg/liter or ppm) of the compound at the temperature of the system,

M_{xi} = Henry's-law constant in atmospheres.

Using Eq. (3), the Henry's-law constant for nitrobenzene at 25°C is calculated in the following manner:

$$M_{xi} = \frac{(73)(0.27)(123)}{2000}$$
$$= 1.21 .$$

B. ESTIMATION OF SECONDARY VOC EMISSIONS FROM WASTEWATER SYSTEMS

As an example, secondary VOC emissions will be estimated for a nonaerated flow system, an aerated flow system, and a nonaerated, nonflow system with nitrobenzene as the model compound.

1. **Nonaerated Flow System**

The model clarifier discussed in Sect. III-B will be used as an example of a nonaerated flow system. For nonaerated systems without biological degradation, such as clarifiers and settling basins, the estimation methods described by Mackay[1] and modified by Dilling[2] should be used in the following manner:

Using the equation developed in ref. 2, recalculate Henry's-law constant:*

$$H_i = \frac{16.04\ P_i^* M_{wi}}{TS_i} \ , \tag{4}$$

where

H_i = Henry's-law constant, dimensionless,
P_i^* = the compound's pure-component vapor pressure in mm Hg at T,
M_{wi} = the molecular weight,
T = the absolute temperature of the wastewater in K,
S_i = the compound's solubility in mg/liter at T.

Then for nitrobenzene:

$$H_i = \frac{16.04(0.27)(123)}{(298)(2000)} = 8.9 \text{ X } 10^{-4} .$$

Calculate the overall liquid mass-transfer coefficient K_{il} by the following equation from ref. 2:

$$K_{il} = \frac{(221.1)(0.6)}{\left(\frac{1.042}{H_i} + 100\right)\left(M_{wi}\right)^{1/2}} \ , \text{ in m/hr,} \tag{5}$$

where H_i is Henry's-law constant, M_{wi} is the molecular weight, and K_{il} is the overall liquid mass-transfer coefficient in m/hr.

Then

$$K_{il} = \frac{(221.1)(0.6)}{\left(\frac{1.042}{8.9 \text{ X } 10^{-4}} + 100\right)(123)^{1/2}} = 9.4 \text{ X } 10^{-3} \ , \text{ in m/hr.} \tag{6}$$

---

*Dilling defines H_i as dimensionless (i.e., mg of chemical per liter of air divided by mg of chemical per liter of water), whereas M_{xi} is in units of atmospheres.

Calculate the percent desorption from the Mackay model (ref. 1):

$$\frac{C_i}{C_o} = \exp\left(-K_{il}\,\frac{t}{L}\right), \tag{7}$$

where

C_i = the concentration at time t of the nitrobenzene,
C_o = the initial nitrobenzene concentration,
L = the liquid depth (in m),
t = the retention time (in hr) of the liquid in the wastewater system.

For a clarifier with a 3-hr retention time and a 3-m depth,

$$\frac{C_i}{C_o} = \exp\left(-9.4 \times 10^{-3}\,\frac{3}{3}\right) = 0.99.$$

The percent desorption is equal to $\left(1 - \frac{C_i}{C_o}\right) \times 100$, or 1%.

Aerated Flow System

For this example the model activated-sludge system discussed in Sect. IV-E and the activated-sludge system model described by Thibodeaux[3] are used.

Thibodeaux's work is basically a paper study using computer simulations for the desorption of oxygen-containing polar compounds from wastewater. Most of the compounds are infinitely soluble in water. Equations are developed for the desorption of these compounds from different wastewater treatment systems, and the desorption values are summarized either in tables or figures. The compounds and associated Henry's-law constants from Thibodeaux's paper are summarized in Table B-1.

Table B-1. Henry's Law Constants from Thibodeaux*

Compound	M_{xi} (atmospheres)
Acetaldeyde	5.88
Acetone	1.99
Isopropanol	1.19
n-Propanol	0.471
Ethanol	0.363
Methanol	0.300
n-Butanol	0.182
Formic acid	0.0247
Propionic acid	0.0130

*See ref. 3.

Table B-2, adapted from Thibodeaux's work,[3] shows the relationship of desorption (secondary VOC emission) versus Henry's-law constant and the ease of biodegradability in an activated-sludge system. In an activated-sludge system easy-to-biodegrade chemicals are not desorbed as much as difficult-to-biodegrade chemicals are.

Table B-2. Desorption as a Function of Henry's-Law Constant in an Activated-Sludge Wastewater Treatment System at 25°C

Henry's-Law Constant M_{xi}	Desorption (%) Of High-Rate Biodegradable Material	Desorption (%) Of Low-Rate Biodegradable Material
5.88	0.41	11.0
1.99	0.13	3.76
1.19	0.055	1.62
0.471	0.023	0.685
0.363	0.022	0.660
0.300	0.025	0.749
0.182	0.0071	0.212
0.0247	0.0021	0.062
0.0130	0.0006	0.019

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The desorption of nitrobenzene (M_{xi} = 1.21) from an activated-sludge system was estimated by interpolation from Table B-2 as 0.06% based on nitrobenzene being easily biodegraded. Within the order-of-magnitude limits of the estimation techniques discussed in this Appendix, the data in Table B-2 can be presented as the following approximate linear equations:

$$\text{\% desorption (high-rate biodegradability)} = 0.07\ M_{xi}\ . \qquad (8)$$

$$\text{\% desorption (low-rate biodegradability)} = 1.87\ M_{xi}\ . \qquad (9)$$

Equations (8) and (9) are used throughout this report to estimate secondary VOC emissions from activated-sludge wastewater treatment systems for chemicals other than those listed in Table B-1. High-rate biodegradable chemicals are those that are easily biodegraded in a typical industrial activated-sludge system. Low-rate biodegradable chemicals are those that are more difficult to biodegrade in a typical industrial activated-sludge system. Examples of low-rate biodegradable chemicals would be certain highly chlorinated organics.

3. Nonaerated Nonflow System

The model surface impoundment discussed in Sect. VI will be used as an example of a nonaerated, nonflow system. The estimation method described by Mackay[1] is used, and has the following bases:

The surface impoundment system is a basin containing an organic liquid or solid that is covered by an aqueous layer.

A steady-state situation exists. The rate of solution of the organic material into the aqueous cover equals the rate of desorption of the organic material into the atmosphere from the aqueous cover.

Sufficient atmospheric dispersion exists above the surface impoundment so that the partial pressure (P_i^*) of the organic material above the aqueous cover is negligible.

The chemical is present in the aqueous cover at the solubility limit concentration (C_s). For nitrobenzene at 25°C, C_s is equal to 2000 Mg/liter. The area of the surface impoundment is 4047 m^2.

The secondary VOC emission (SE_{sa}) from the aqueous cover into the atmosphere is obtained from the following equation by Dilling[2] from Mackay's model:

$$SE_{sa} = K_{il} \left(C_s - \frac{P_i^*}{H_i} \right) . \qquad (8)$$

Since P_i^* is negligible, Eq. (8) reduces to

$$SE_{sa} = K_{il} C_s \quad , \qquad (9)$$

where

SE_{sa} = the secondary VOC emission rate from the surface impoundment in $g/(m^2)(hr)$,

K_{il} = the overall liquid-phase mass transfer coefficient in m/hr,

C_s = the chemical concentration in the aqueous cover in mg of chemical per liter of wastewater (mg/liter is equivalent to g/m^3).

For nitrobenzene (NB) at 25°C SE_{sa} is calculated in the following way:

$$SE_{sa} = (9.4 \text{ X } 10^{-3} \text{ m/hr})(2000 \text{ g of NB/m}^3 \text{ of WW})$$

$$= 18.8 \text{ g of NB per hr per m}^2 \text{ of wastewater.}$$

For 4047 m^2 of surface impoundment area and 8760 hr/yr the secondary VOC emission rate becomes 667 Mg of nitrobenzene secondary emissions per year.

C. GENERAL COMMENTS ON THE PROCEDURES FOR ESTIMATING SECONDARY VOC EMISSIONS

The procedures used in this Appendix for estimating the secondary VOC emissions should be considered as only an order-of-magnitude estimate for the following reasons:

1. They are based on a pure-component analysis and do not incorporate any possible chemical interreaction, hydrolysis, or acid/base caused reactions, such as the conversion of phenol to sodium phenate.
2. The Thibodeaux work[3] is a theoretical analysis based mostly on average parameters obtained from the literature.
3. The Thibodeaux simulation[3] does not take into account, for instance, absorption of organics on sludge and/or other suspended solids in the wastewater.

The simulation also does not account for possible desorption of biochemical reaction products or organic degradation via catalyzed or uncatalyzed photodegradation.

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APPENDIX C

ESTIMATE OF UNCONTROLLED SECONDARY VOC EMISSIONS FROM WASTEWATERS FOR THE SYNTHETIC ORGANIC CHEMICALS MANUFACTURING INDUSTRY (SOCMI)

Appendix C

ESTIMATE OF UNCONTROLLED SECONDARY VOC EMISSIONS FROM WASTEWATERS FOR THE SOCMI

Data on secondary VOC emissions from wastewater for the SOCMI are very limited. Therefore an order-of-magnitude theoretical assessment has been made based on available SOCMI wastewater data and on the model chemical production plant and the model wastewater treatment systems described in Sect. IV-E.

The wastewater data used are from the 30 highest volume SOCMI chemical products.[1—4] The model clarifier emissions were estimated based on the Mackay[5] and Dilling[6] methods as discussed in Appendix A. The model activated-sludge system emissions were estimated based on the Thibodeaux[7] method modified as discussed in Appendix B.

A. CRITERIA

The following criteria were used in the estimations:

The wastewater from the production of each chemical enters a model-plant wastewater treatment system at 20 or 25°C, which includes, in series, a 3-hr retention time, a 3-m-deep clarifier, and an activated-sludge system.

Wastewater total organic carbon (TOC), chemical oxygen demand (COD), and flow parameters were average values taken from refs. 1—4 for the major process given in the reference.

All wastewater TOC and COD were attributed to only the chemical produced.

In cases where, at 20 or 25°C, the solubility of the chemical produced was lower than that of the process TOC or COD data, the chemical solubility was used in making the estimate.

The desorption of each chemical in the model-plant wastewater treatment system was calculated based on estimated Henry's-law constants and the procedures described in Appendix B.

B. ESTIMATION OF WASTEWATER PRODUCT CONCENTRATION

Table C-1 summarizes the estimation of the wastewater product concentration for each of the 30 products listed.

Column A summarizes the average amount of wastewater TOC or COD per Mg of wastewater for each product.

Column B is the theoretical ratio of the molecular weight of the product to the TOC or COD for each mole of chemical listed. For example, the molecular weight ratio of ethylene to organic carbon is 28:24, or 1.17.

Multiplication of column A by column B results in column C, the amount of the product present, in grams, per Mg of wastewater. Column C in Table C-1 is compared with column E in Table C-2 (the product solubility at 20 or 25°C), and the smaller of the two is used in the next estimation.

C. ESTIMATION OF THE AMOUNT OF PRODUCT DESORBED (D_T) FROM THE MODEL-PLANT WASTEWATER SYSTEM

Using the procedures described in Appendix A, Henry's-law constants (M_{xi} and H_i) and the overall liquid mass-transfer coefficients (K_{il}) were estimated for each product and used to estimate the desorption fraction (D_c) for the clarifier and the activated-sludge system (D_a) (see Table C-2).

The total desorption fraction (D_T) is the sum of D_c and $D_a(1 - D_c)$ and is defined as the amount (in grams) of product desorbed from the wastewater per gram of product originally present in the wastewater.

D. ESTIMATION OF THE SOCMI UNCONTROLLED SECONDARY VOC EMISSION FACTOR (SE_f)

Column D in Table C-1 summarizes the average amount of wastewater (WW) used to make 1 g of each product.

Multiplication of column D by D_T and the smaller of column C or E results in the secondary VOC emission factors (SE_f) for the products shown in Table IV-4. For ethylbenzene (EB), SE_f would be estimated as follows:

$$SE_f = \frac{0.31 \text{ g of WW}}{\text{g of EB produced}} \times \frac{0.34 \text{ g of EB desorbed}}{\text{g of EB in WW}} \times \frac{152 \text{ g of EB in WW}}{\text{Mg of WW}}$$

$$= 16 \text{ g of EB desorbed per Mg of EB produced.}$$

Table C-1. Wastewater Parameters

Chemical	(Col A) g of TOC (in WW) / Mg of WW	(Col B) g of Prod. / g of TOC	(Col C) g of Prod. (in WW) / Mg of WW	(Col D) g of WW / g of Prod.	Data Source for Cols A and D
Ethylene	758	1.17	887	1.71	Ref. 1
Ethylene dichloride	1,106	4.08	4,516	0.80	Ref. 1
Styrene	22	1.08	24	14.50	Ref. 1
Methanol	345	2.67	920	0.42	Ref. 1
Ethylbenzene	2,091	1.10	2,300	0.31	Ref. 1
Vinyl chloride	120	2.60	313	2.80	Ref. 1
Ethylene oxide	11,175	1.83	20,487	0.62	Ref. 1
Ethylene glycol	929	2.58	2,400	4.87	Ref. 1
1,3-Butadiene	502	1.13	564	1.70	Ref. 1
Dimethylterephthalate	4,606	1.62	7,446	4.24	Ref. 1
Cumene	180	1.11	200	3.3×10^{-4}	Ref. 2
Acetic acid	3,843[a]	0.94[a]	3,600	2.1	Ref. 1
Cyclohexane				0.002	Ref. 1
Phenol	38,800[a]	0.81[a]	31,337	1.85	Ref. 1
Chlorinated methanes	198	8.52	1,686	1.33	Ref. 2
Isopropal alcohol	519	1.67	865	2.54	Ref. 2
Acetone	38,800[a]	0.62	23,862	3.00	Ref. 1
Propylene oxide	345	1.61	556	61.26	Ref. 2
Acetic anhydride	153,140[a]	0.80	122,031	2.13	Ref. 3
Acrylonitrile	19,633	1.47	28,900	4.20	Ref. 2
Ethanol	30,000[a]	0.48	14,375	2.80[b]	Ref. 3
Vinyl acetate	220	1.79	394	0.23	Ref. 1
Terephthalic acid	10	1.73	17	4.24	Ref. 1
Adipic acid				[c]	
t-Butanol	19,483[b]	1.54	30,036	19.1[b]	Ref. 2
Acetaldehyde	18,560	1.57	29,166	0.52	Ref. 1
Cyclohexanol/cyclohexanone	580	1.38	800	1.15	Ref. 4
Phthalic anhydride	26,217	1.54	40,418	1.44	Ref. 2
Adiponitrile	4,500	1.50	6,750	9.76	Ref. 2
Caprolactam	109	1.57	171	11.13	Ref. 1

[a] COD. [b] Estimate. [c] Essentially zero secondary VOC emission rate.

Table C-2. Summary of VOC Desorption Calculations

	Parameters[a]								
Chemical	(Col E) F_i	P_i^*	M_i	H_i	K_{ij}	D_c	M_{xi}	D_a	D_T
Ethylene	131	30,400	28	356	0.25	0.22	474,300	1.0	1.0
Ethylene dichloride	8690	61	99	0.038	0.105	0.10	51	0.66	0.69
Styrene	300	5	104	0.095	0.117	0.11	127	0.09	0.19
Methanol	Inf.	123	32	2.3×10^{-4}	5×10^{-3}	0.005	0.3	0	0.005
Ethylbenzene	152	7	106	0.267	0.124	0.12	356	0.25	0.34
Vinyl chloride	1100	2660	62.5	8.3	0.168	0.15	11,030	1.00	1.0
Ethylene oxide	Inf.	1095	44	8.2×10^{-3}	0.088	0.084	11	0.008	0.09
Ethylene glycol	Inf.	0.05	62	4.3×10^{-7}	6.9×10^{-6}	0	5.8×10^{-4}	0	0
1,3-Butadiene	735	1900	54	7.6	0.18	0.17	10,190	1.00	1.00
Dimethylterephthalate	<19	0.011	194	6×10^{-3}	0.035	0.034	8	0.005	0.04
Cumene	50	3.2	120	0.419	0.118	0.11	560	0.39	0.46
Acetic acid	Inf.	11.4	60	4.6×10^{-5}	7.6×10^{-4}	0	0.063	0	0
Cyclohexane	55	77	84	6.4	0.145	0.14	8,585	1.00	1.0
Phenol	82,000	0.2	94	2.2×10^{-5}	3.6×10^{-4}	0	0.03	0	0
Chlorinated methanes	5894	986	112.4	1.01	0.124	0.12	1373	1.00	1.0
Isopropal alcohol	Inf.	32	60	8.8×10^{-4}	0.0133	0.013	1.19	0.001	0.014
Acetone	Inf.	179	58	1.5×10^{-3}	0.0215	0.021	1.99	0.001	0.022
Propylene oxide	405,000	400	58	7.4×10^{-3}	0.072	0.07	10	0.007	0.077
Acetic anhydride	Inf.	3.5	102	7.4×10^{-5}	9.2×10^{-4}	0.001	0.1	0	0.001
Acrylonitrile	73,500	100	53	4.8×10^{-3}	0.057	0.055	6.5	0.004	0.06
Ethanol	Inf.	43.9	46	2.6×10^{-4}	4.9×10^{-3}	0.005	0.36	0	0.005
Vinyl acetate	20,000	83	86	0.0194	0.093	0.09	26	0.018	0.11
Terephthalic acid	19	5×10^{-6}	166	2.3×10^{-6}	2.3×10^{-5}	0	3×10^{-3}	0	0
Adipic acid	15,000	1×10^{-4}	146	5.3×10^{-8}	5.6×10^{-7}	0	7×10^{-5}	0	0
t-Butanol	Inf.	31	74	3.3×10^{-4}	4.7×10^{-3}	0.005	0.45	0	0.005
Acetaldehyde	Inf.	740	44	4.3×10^{-3}	0.0587	0.057	5.88	0.004	0.06
Cyclohexanol/ cyclohexanone	30,000	2.3	99	4.8×10^{-4}	6.1×10^{-3}	0.006	0.65	0	0.006
Phthalic anhydride	6200	2×10^{-4}	148	2.6×10^{-7}	2.7×10^{-6}	0	3.5×10^{-4}	0	0
Adiponitrile	30,000	1×10^{-3}	108	1.9×10^{-7}	2.4×10^{-6}	0	2.6×10^{-9}	0	0
Caprolactan	840,000	1×10^{-3}	113	7.2×10^{-9}	8.6×10^{-9}	0	9.8×10^{-6}	0	0

[a] See Sect. E in this appendix for definition.

Multiplication of SE_f by the estimated 1978 production[8] results in an estimate of secondary VOC emissions for each product (Table IV-4). The sum of these estimated emissions (35.7 Gg) divided by the total production (54,600 Gg) results in an estimated average SOCMI uncontrolled secondary VOC wastewater emission factor of 650 g of VOC per Mg of product produced.

Multiplication of the SOCMI emission factor (650 g/Mg) by the total SOCMI 1978 production (100,000 Gg) results in an estimated 65 Gg/yr of uncontrolled secondary emissions from wastewater.

E. SYMBOLS AND DEFINITIONS

The symbols that are used in this Appendix are defined below:

Symbol	Definition
S_i	Solubility of the product in water, generally at ambient temperature (mg/liter or g of product per Mg of WW)
P_i^*	Pure-component vapor pressure of product at 20 or 25°C (mm Hg)
M_{wi}	Molecular weight of product
H_i	Henry's-law constant: mg of chemical per liter of air ÷ mg of chemical per liter of water (see Appendix A)
K_{il}	Overall liquid mass-transfer coefficient as defined in Appendix A
D_c	Mass fraction of VOC desorbed in the clarifier of the model-plant wastewater treatment system
M_{xi}	Henry's-law constant in atmospheres
D_a	Mass fraction of VOC desorbed in the activated-sludge system of the model-plant wastewater treatment system
D_T	Total mass fraction of VOC desorbed in the total model-plant wastewater treatment system; defined as D_c plus $D_a(1 - D_c)$

F. REFERENCES*

1. Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Major Organic Products Segment of the Organic Chemicals Manufacturing Point Source Category, EPA 440/1-74-009-a (April 1974).

2. Development Document for Interim Final Effluent Limitations Guidelines and New Source Performance Standards for the Significant Organic Products Segment of the Organic Chemical Manufacturing Point Source Category, EPA 440/1-75-045, Group I, Phase II (November 1975).

3. Monsanto Research Corp. and Research Triangle Institute, Chapter 6. The Industrial Organic Chemicals Industry, Part I.

4. W. D. Bruce, IT Enviroscience, Inc., Trip Report for Visit to Monsanto Textiles Co., Pensacola, FL, Feb. 8, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

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6. W. L. Dilling, "Interphase Transfer Processes," Environmental Science and Technology 11(4), 405—409 (April 1977).

7. L. J. Thibodeaux, "Air Stripping of Organics from Wastewater. A Compendium," pp. 358—378 in the Proceedings of the Second National Conference on Complete Watereuse. Water's Interface with Energy, Air and Solids, Chicago, IL, May 4—8, 1975, sponsored by AIChE and EPA Technology Transfer.

8. Synthetic Organic Chemicals, 1976 United States Production and Sales, United States International Trade Commission, GPO, Washington (1977).

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

APPENDIX D

COMPARISON OF SECONDARY VOC EMISSIONS FOR FIVE MODEL CHEMICALS

Appendix D

COMPARISON OF SECONDARY VOC EMISSIONS FOR FIVE MODEL CHEMICALS

Data on the secondary VOC emissions of chemicals in a landfill are limited.[1] Because of this scarcity an assessment of the secondary VOC emissions from landfills and wastewater treatment was done. This assessment is a theoretical order-of-magnitude analysis that compares the secondary VOC emissions for five model compounds: hexachlorobenzene, paradichlorobenzene, benzene, acetone, and acetic acid. The compounds encompass a wide range of physical properties.

The Mackay,[2] Dilling,[3] Thibodeaux,[4] and Farmer[5] models were used for estimating the secondary VOC emissions.

The bases and calculations used in the estimation and comparison of the secondary VOC emissions from the wastewater system with those from the landfill are as follows:

A. PHYSICAL PROPERTIES OF MODEL CHEMICALS AT 25°C

The physical properties used in the estimation of the secondary VOC emissions from the treatment systems are given in Table D-1.

Table D-1. Physical Properties of Model Chemicals

Compound	Hexachlorobenzene	p-Dichlorobenzene	Benzene	Acetone	Acetic acid
Abbreviation	HCB	DCB	Bz	A	HAC
Vapor pressure (mm Hg)	1.9×10^{-5}	1.0	95.2	220	11.4
Molecular weight	285	147	78	58	60
Solubility in water (mg/liter)	0.0062	79	1790 [4]	Inf.	Inf.

B. CALCULATION OF HENRY'S LAW CONSTANTS AND K_{il}

Henry's-law contants H_i (Dilling[3]) and M_{xi} (Thibodeaux[4]) and the overall liquid mass-transfer coefficient K_{il} for HCB, DCB, and Bz were calculated based on the procedures discussed in Appendix B. The results are summarized in Table D-2.

Table D-2. Calculated Properties of Model Chemicals

Constant	HCB	DCB	Bz	A	HAC
H_i (mg of chemical per liter of air ÷ mg of chemical per liter of water)	0.047	0.100	0.224	1.5×10^{-3}	4.6×10^{-5}
K_{il} (m/hr)	0.064	0.099	0.144	0.022	7.6×10^{-4}
M_{xi} (atm)	64	136	303	1.99	0.06

The M_{xi} values for acetone and acetic acid were obtained from ref. 4. The H_i and K_{il} values for acetone were estimated from the following relationships:

$$M_{xi} = \frac{73\, P_i^* M_{wi}}{S_i} \quad , \tag{1}$$

and

$$H_i = \frac{16.04\, P_i^* M_{wi}}{T S_i} \quad . \tag{2}$$

Dividing Eq. (1) by Eq. (2) results in the following approximate relationship between H_i and M_{xi}:

$$M_{xi} = \frac{73\, TH_i}{16.04} \quad .$$

Then, for $T = 298$ K, $M_{xi} = 1356\, H_i$. (3)

C. ESTIMATION OF SECONDARY VOC EMISSIONS FOR A CLARIFIER (SE_c)

The following bases were used for calculation of the secondary VOC emissions for the model wastewater treatment plant:

The clarifier is 3 m deep, has a surface area of 700 m^2, and has a retention time of 3 hr.

The wastewater flow is 17,000 m^3/day.

For the HCB, DCB, and Bz calculations the wastewater will be saturated at the solubility limit of each chemical at 25°C.

For the acetone and acetic acid calculations the concentration used is 1360 mg/liter (see Table IV-3).

The percent desorption (D_c) of the chemical from the wastewater in the clarifier is calculated from the Mackay model [Appendix A, Eq. (7)].

After the percent desorption (D_c) of each chemical was obtained, the secondary VOC emissions from the clarifier (SE_c) were calculated. For example, for acetone:

$$SE_a = \frac{17{,}000 \text{ m}^3 \text{ of WW}}{\text{day}} \times \frac{365 \text{ days}}{\text{yr}} \times \frac{1 \text{ Mg of WW}}{\text{m}^3 \text{ of WW}} \times \frac{1360 \text{ g of acetone in WW}}{\text{Mg of WW}} \times$$

$$\times \frac{0.022 \text{ g of acetone as secondary emission}}{\text{g of acetone in WW}}$$

$$= 186 \text{ Mg of acetone as secondary emissions per year.}$$

. ESTIMATE OF SECONDARY VOC EMISSIONS FOR AN ACTIVATED-SLUDGE WASTEWATER TREATMENT SYSTEM (SE_a)

The following bases were used for calculating the secondary VOC emissions (SE_a) from the model activated-sludge system:

The activated-sludge system in 6 m deep and has a surface area of 6300 m^2.

The wastewater flow is 17,000 m^3/day.

The wastewater chemical concentrations into the activated-sludge system are based on the clarifier inlet concentrations less the amount of secondary emissions of that chemical from the clarifier.

The percent desorption (D_a) of a chemical from the wastewater in the activated-sludge system is estimated from the Thibodeaux model[4] discussed in Appendix A.

The estimation of the SE_a for the model chemicals is based on HCB being difficult to biodegrade and on Bz, HAC, and A being easy to biodegrade. The SE_a for DCB was estimated with both types of biodegradability to show the relative importance of the biodegradability parameter.

After the percent desorption (D_a) was obtained for each chemical [Eqs. (8) and (9) in Appendix A] SE_a was calculated. For example, for benzene

$$SE_a = \frac{17{,}000 \text{ m}^3 \text{ of WW}}{\text{day}} \times \frac{365 \text{ days}}{\text{yr}} \times \frac{1 \text{ Mg of WW}}{\text{m}^3 \text{ of WW}} \times \frac{1550 \text{ g of benzene in WW}}{\text{Mg of WW}} \times$$

$$\times \frac{0.21 \text{ g of benzene as secondary emission}}{\text{g of benzene in WW}}$$

$$= 2020 \text{ Mg of benzene as secondary emissions per year.}$$

E. ESTIMATE OF SECONDARY VOC EMISSIONS FOR A LANDFILL (SE_1)

The following bases were used in the estimations:

The soil in the landfill is dry, having no moisture content.

There is no water movement through soil.

The soil bulk density is 1.2 g/cm^3.

The soil particle density is 2.65 g/cm^3.

The depth of soil cover is 0.6 m.

There is no biological decomposition of the chemical in soil.

There are no cracks or other small openings in the soil cover.

The secondary VOC emission, in kg/(m^2)(yr), is calculated from the Farmer model.[5]

The landfill usage rate is 4047 m^2 per year.

The estimation of the organic vapor from a landfill is obtained from the following equation:

$$SE_{1a} = \frac{D_i C_s \left(P_t\right)^{4/3}}{L} , \tag{4}$$

where

SE_{1a} = the secondary VOC emission from the landfill [kg/(yr)(m^2)],
D_i = the chemical's vapor diffusion coeffient in air (m^2/yr),
C_s = the concentration of volatilizing material in air or the vapor density at the bottom of the soil cover (kg/m^3),
P_t = the total soil porosity (m^3/m^3),
L = the soil cover depth (m).

D_i, C_s, and P_t are estimated from Eqs. (5a), (5b), and (5c):

$$D_i = D_{HCB}\left(\frac{M_{wHCB}}{M_{wi}}\right)^{1/2} , \tag{5a}$$

where

D_{HCB} = the experimentally derived vapor diffusion coefficient of hexachlorobenzene;
M_{wHCB} = the molecular weight of HCB;
M_{wi} = the molecular weight of the compound to be estimated;

$$C_s = \frac{P_i^* M_{wi}}{RT} , \tag{5b}$$

where

P_i^* = the pure-component vapor pressure;
M_{wi} = the molecular weight;
R = the gas constant;
T = the temperature;

$$P_t = 1 - \frac{B}{P} , \tag{5c}$$

where B is the soil bulk density and P is the soil particle density.

Combining Eq. (4) with Eqs. (5a), (5b), and (5c) results in the following estimation equation at 25°C:

$$SE_{1a} = 0.148\ P_i^* \frac{(M_{wi})^{1/2}}{L}\ , \qquad (6)$$

where

P_i^* is in mm Hg at 25°C,
L is in meters,
SE_{1a} is in kg/(yr)(m^2).

Equation (6) gives a conservatively high estimate of emissions because of the bases used in the estimate.

The secondary VOC emission rate is calculated by multiplying Eq. (6) by the annual landfill usage rate of 4047 m^2, dividing by the soil cover depth of 0.6 m, and converting to Mg per year:

$$SE_1 = \frac{0.148 \times 4047\ P_i^*(M_{wi})^{1/2}}{0.6\ (1000)}$$

$$= 1\ P_i^*(M_{wi})^{1/2},$$

where SE_1 is in Mg/yr.

The landfill secondary emission for DCB, for example, is calculated as follows:

$$SE_1 = (1)(1)(147)^{1/2}$$

$$= 12 \text{ Mg of DCB secondary emissions per year.}$$

G. COMPARISON OF SECONDARY VOC EMISSIONS

Comparisons are made in Table IV-6 for both the secondary VOC emissions for 5 model chemicals and for the emissions from a wastewater treatment plant vs those from a landfill.

G. REFERENCES*

1. R. Markle, R. B. Iden, and F. A. Sliemers, "Preliminary Examination of Vinyl Chloride Emissions from Polymerization Sludges During Handling and Land Disposal," pp. 186—194 in Residual Management by Land Disposal. Proceedings of the Hazardous Waste Research Symposium, edited by W. H. Fuller, EPA-600/9-76-015 (July 1976).

2. D. Mackay and P. J. Leinonen, "Rate of Evaporation of Low-Solubility Contaminants from Water Bodies to Atmosphere," Environmental Science and Technology 9(13), 1178—1180 (December 1975).

3. W. L. Dilling, "Interphase Transfer Processes," Environmental Science and Technology 11(4), 405—409 (April 1977).

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5. W. J. Farmer and M. H. Roulier, "Land Disposal of Hexachlorobenzene Wastes: Controlling Vapor Movement in the Soil," p. 182 in the Fourth Annual Research Symposium on Land Disposal of Hazardous Waste, San Antonio, TX, March 6—8, 1978, sponsored by the Southwest Research Institute and the EPA.

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APPENDIX E

COST CALCULATIONS FOR VOC SECONDARY EMISSION CONTROL OPTIONS

Appendix E

COST CALCULATIONS FOR VOC SECONDARY EMISSION CONTROL OPTIONS

The calculations for the estimated costs and cost effectiveness for the control of secondary VOC emission are presented in this Appendix. The cost estimates are based on a model plant. Details of the model plant are given in Tables IV-2, IV-3, IV-5, and E-1.

Table E-1. Parameters for Model-Plant Surface Impoundment

Surface impoundment area (m^2)	4047
Chemical A solubility (Mg/liter) at 25°C	0.0062
Chemical B solubility (Mg/liter) at 25°C	79
Uncontrolled secondary VOC emissions	
Chemical A (Mg/yr)	0.014
Chemical B (Mg/yr)	277

Capital cost estimates represent the total investment required for purchase and installation of all equipment and material needed for a complete emission control system performing as defined for a new plant at a typical location. These estimates do not include the cost of research and development, land acquisition, or production lost during installation or startup. The primary difficulty in retrofitting may be in finding space to fit the system into the existing plant layout. Because of these associated costs the cost of retrofitting emission control systems in existing plants may be appreciably greater than that for a new installation.

Bases for the annual cost estimates for the control alternatives include utilities, waste disposal, raw materials, operating labor, recovery and disposal credits, capital-related charges, and miscellaneous recurring costs such as taxes, insurance, and administrative overhead. The cost factors used are itemized in Table E-2. The capital recovery factor of 0.18 is based on an assumed 10-year life and a 12% annual interest rate. Annual costs are for a 1-year period beginning in December 1979.

Table E-2. Cost Factors Used for Computing Annual Costs

Utilities	
Natural gas	$1.90/GJ
Electricity	$0.00833/MJ ($0.03/kWh)
Maintenance material and labor	0.06 X capital cost
Capital charges	
Capital recovery	0.18 X capital cost
Misc. (taxes, insurance, administration)	0.05 X capital cost
Recovery credits	
Chemical	$0 to 0.36 per kg
Energy	$1.90/GJ
Chemical disposal charges	$0.12/kg

A summary of the control option cost estimates is shown in Table E-3. These net annual costs were used in calculating the cost effectiveness of each option.

A. CONTROL OPTION 1——RESOURCE RECOVERY BY CARBON ADSORPTION OF THE MODEL-PLANT WASTEWATER

1. Bases Used in the Calculations

The wastewater parameters are those described in Table IV-3.

A carbon adsorption system is used to remove 99 wt % of the VOC from the wastewater; the remainder (84.4 Mg/yr) enters the model-plant wastewater treatment system (see Table IV-2 and Fig. VI-1).

The carbon adsorption parameters are as follows:

Carbon loading	0.1 g of VOC per g of carbon
Steam for regeneration	10 g/g of organic absorbed
Cooling water for the steam/VOC condenser	1.4 M m^3/yr
Granular activated carbon replacement every 2 yr	$2.58/kg
Carbon loading cycle time	10 hr

Table E-3. Cost Estimates for Control of Secondary VOC Emissions for Model Plant

Cost Item	Total Installed Capital Cost	Annual Operating Cost, December 1979					Net Annual Costs	Emission Reduction		Effectiveness[b]
		Utilities and Raw Materials	Manpower	Capital Related Costs	Contract Waste Disposal Costs	Recovery (Credits)[a]		(Mg/yr)	(%)	(per Mg)
Wastewater										
Carbon adsorption (CA)[c]	$3,900,000	647,000	39,400	1,131,000			$1,817,400	1049	99	$ 1,733
Cover for clarifier[d]	75,320			21,840			21,840	903	85	24
Cover and CA with chemical recovery[e]	1,363,200	25,700	39,400	395,300		(26,300)	434,100	1049	99	414
Cover and CA without chemical recovery[c]	1,363,200	25,700	39,400	395,300	$17,500		477,900	1049	99	456
Cover and fume incineration (FI) without energy recovery[f]	1,583,200	909,300	27,000	459,100			1,395,400	1049	99	1,330
Cover and FI with energy recovery[f]	2,153,200	910,100	27,000	624,400		(598,700)	962,800	1049	99	918
Landfill										
Cover/chemical A[g]	435,600			126,300			126,300	3×10^{-4}	99	420,000,000
Cover/chemical B[h]	435,600			126,300			126,300	12	99	10,500
Surface impoundment										
Cover/chemical A[g]	435,600			126,300			126,300	0.014	99	9,000,000
Cover/chemical B[h]	435,600			126,300			126,300	274	99	460

[a] Net annual cost and cost effectiveness depend strongly on recovery credits.

[b] Cost per Mg of VOC emission reduction.

[c] See Fig. VI-1.

[d] See Fig. VI-2.

[e] See Fig. VI-3.

[f] See Fig. VI-4.

[g] Low-vapor-pressure solid.

[h] High-vapor-pressure solid.

The chemical recovery credit was estimated as follows: The production-weighted average selling price for chemicals shown in Table C-1, based on the Oct. 9, 1978, issue of the Chemical Marketing Reporter, was $0.36/kg. The recovered value of the chemical from the model industry was then varied from zero to $0.36 per kg of recovered chemical.

2. Calculation of Costs and Cost Effectiveness

The net annual costs were calculated to be $1,817,400 (see Table E-3).

The uncontrolled VOC secondary emissions from the wastewater were calculated to be 1060 Mg/yr. The controlled VOC secondary emissions with the use of control option 1, resource recovery, were calculated to be 11 Mg/yr. The total VOC reduction was calculated as 99%.

The cost effectiveness was calculated to be $1733/Mg ($1,817,400 ÷ 1049 Mg of VOC emission reduction).

B. CONTROL OPTION 2——FLOATING PLASTIC COVER FOR MODEL CLARIFIER

1. Bases Used in the Calculations

The parameters for the model plant and those for the model-plant wastewater treatment system are described in Tables IV-2 and IV-3.

The control option consists of a plastic cover on the clarifier but not on the activated-sludge system.

No secondary VOC control system is used for the activated-sludge system.

The total installed capital cost of the floating gas-tight plastic cover is $107.60/m^2 (ref. 1).

The life of the plastic covers is 10 years.

Uncontrolled secondary VOC emissions from the model-plant wastewater treatment system are 1060 Mg/yr.

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The secondary VOC emissions from the clarifier are reduced 99% by the floating gas-tight plastic cover.

2. Calculation of Costs and Cost Effectiveness

The net annual costs were calculated to be $21,840 (see Table E-3).

The uncontrolled secondary VOC emissions of 1060 Mg were reduced by 85% to 157 Mg of secondary VOC emissions per year.

The cost effectiveness was calculated to be $24/Mg ($21,840 ÷ 903 Mg) of VOC emission reduced).

C. CONTROL OPTION 3——CARBON ADSORPTION WITH AND WITHOUT CHEMICAL RECOVERY OF THE VOC SECONDARY EMISSIONS FROM A CONVENTIONAL ACTIVATED-SLUDGE (CAS) SYSTEM

1. Bases Used in the Calculations

The parameters for the model plant and those for the model wastewater treatment system are as described in Tables IV-2 and IV-3.

Gas-tight floating plastic covers are used on the clarifier and CAS system. The cover on the clarifier results in a VOC reduction of 99%. The CAS off-gas is vented to a carbon adsorption system as shown in Fig. VI-3.

The CAS off-gas is saturated with water vapor at 32.2°C and has the following composition and flow rate:

	Amount (vol %)	Rate (kg/hr)
Carbon dioxide	1.6	1,130
Oxygen	17.4	8,751
Nitrogen	76.4	33,640
Water	4.6	1,306
VOC	185 (ppm)	17
	100.0	44,844

The actual volumetric flow rate at 32.2°C is 657 m^3/min.

Uncontrolled secondary VOC emissions from the clarifier and CAS system are calculated to be 1060 Mg/yr.

The following carbon adsorption parameters were used:

Carbon loading	0.05 g of VOC per g of carbon
Steam for regeneration	20 g/g of organic absorbed
Cooling water for the steam/VOC condenser	69 km^3/yr
Cost of granular activated carbon replacement every 2 yr	\$2.57/kg (\$1.17/lb)
Carbon loading cycle time	8.5 hr

The chemical recovery credit was estimated as follows: The production-weighted average selling price for the chemicals shown in Table IV-3 was \$0.36/kg; the recovered value of the chemical from the model was then varied from zero to \$0.36 per kg.

For the option without chemical recovery the contract waste disposal charge for the recovered chemical was \$0.12/kg.

2. Calculation of Costs and Cost Effectiveness

The net annual costs for the control option with chemical recovery at \$0.18/kg were calculated to be \$434,200 (see Table E-3).

The net annual costs for the control option without chemical recovery were calculated to be \$478,000 (see Table E-3).

The annual uncontrolled VOC secondary emissions from the clarifier and CAS system amount to 1060 Mg. The annual controlled VOC secondary emissions are 11 Mg (see Fig. VI-3). The total annual VOC reduction is 1049 Mg.

The cost effectiveness with chemical recovery was calculated to be \$414/Mg (\$430,000 ÷ 1049 Mg of VOC emission reduced) and without chemical recovery to be \$456/Mg (\$478,000 ÷ 1049 Mg of VOC emission reduced).

D. CONTROL OPTION 4——FUME INCINERATION WITH AND WITHOUT ENERGY RECOVERY OF THE VOC SECONDARY EMISSIONS FROM A CAS SYSTEM

1. Bases Used in the Calculations

The parameters for the model plant and those for the model wastewater treatment system (CAS) are as described in Tables IV-2 and IV-3.

Gas-tight floating plastic covers are used on the clarifier and on the CAS system. The clarifier cover reduces the VOC emissions by 99%. The CAS off-gas is vented to a fume incineration system.

The CAS off-gas is saturated with water vapor at 32.2°C and has the following composition and flow rate:

	Amount (vol %)	Rate (kg/hr)
Carbon dioxide	1.6	1,130
Oxygen	17.4	8,751
Nitrogen	76.4	33,640
Water	4.6	1,306
VOC	185 (ppm)	17
	100.0	44,844

The actual volumetric flow rate at 32.2°C is 657 m^3/min.

The total uncontrolled VOC secondary emissions from the clarifier and CAS system are 1060 Mg/yr.

The VOC has a heat of combustion of 23.3 MJ/kg.

The following fume incineration parameters were used:

Incineration temperature	871°C
Incineration residence time	0.5 sec
Fume energy content	0.1 MJ/m^3
Auxiliary fuel	Natural gas

Oxygen out stack	≥3 mole %
Energy recovery	As steam
Boiler outlet temperature	260°C
VOC	Essentially all C, H, and O
VOC destruction efficiency	>99 wt %

An energy credit of $1.90/GJ was used.

2. Calculation of Costs and Cost Effectiveness

The net annual costs for the control option with energy recovery were calculated to be $962,800 (see Table E-3).

The net annual costs for the control option without energy recovery were calculated to be $1,395,400 (see Table E-3).

The annual uncontrolled VOC secondary emissions from the clarifier and CAS system are 1060 Mg. The annual controlled VOC secondary emissions are 11 Mg (see Fig. VI-4). The total VOC reduction is 99.0%.

The cost effectiveness with energy recovered was calculated to be $918/Mg ($962,800 ÷ 1049 Mg of VOC emission reduced) and without energy recovery to be $1330/Mg ($1,395,400 ÷ 1049 Mg of VOC emission reduced).

E. USE OF PLASTIC COVER TO REDUCE VOC SECONDARY EMISSIONS FROM A LANDFILL

1. Bases Used in the Calculations

Two model chemicals are evaluated, chemical A, with physical properties similar to those of hexachlorobenzene, and chemical B, with physical properties similar to those of *p*-dichlorobenzene, with a 0.6-m-deep soil cover (see Table IV-5).

The secondary VOC emissions for these chemicals are 3.2×10^{-4} Mg of VOC emissions per year for chemical A and 12 Mg of VOC emissions per year for chemical B.

The capital cost of the plastic cover is $107.60/m^2 (ref. 1).

The secondary VOC emissions are reduced 99% by the plastic cover.

The area of the landfill cell to be covered is 4047 m^2 per year.

2. Calculation of Costs and Cost Effectiveness

The net annual costs were calculated to be $126,300 for each chemical (see Table E-3).

The reductions in VOC secondary emissions for chemicals A and B are as follows:

Uncontrolled secondary VOC emissions (Mg/yr)	
Chemical A	3.2×10^{-4}
Chemical B	12
Controlled secondary VOC emissions (Mg/yr)	
Chemical A	3.2×10^{-6}
Chemical B	0.12
Secondary VOC emission reduction (Mg/yr)	
Chemical A	3.17×10^{-4}
Chemical B	11.88

The cost effectiveness for chemical A (see Table E-3) was calculated to be $420,000,000/Mg ($126,300 ÷ 3×10^{-4} Mg of VOC emission reduced) and for chemical B (see Table E-3) was calculated to be $10,500/Mg ($126,300 ÷ 12 Mg of VOC emission reduced).

F. USE OF PLASTIC COVER TO REDUCE VOC SECONDARY EMISSIONS FROM A SURFACE IMPOUNDMENT (SI)

1. Bases Used in the Calculations

Two chemicals are evaluated: model chemical A with physical properties similar to those of hexachlorobenzene and model chemical B with physical properties similar to those of p-dichlorobenzene.

The secondary VOC emissions for these chemicals were calculated using the following bases:

(a) The model-plant surface impoundment system is a basin containing an organic liquid or solid that is covered by an aqueous layer (see Table E-1).

(b) A steady-state situation exists. The rate of solution of the organic material into the aqueous cover equals the rate of desorption of the organic material into the atmosphere from the aqueous cover.

(c) Sufficient atmospheric dispersion exists above the surface impoundment so that the partial pressure (P_i^*) of the organic material above the aqueous cover is negligible.

(d) The concentrations of the organic materials in the aqueous cover are the solubility limits for model chemical A (0.0062 mg/liter) and model chemical B (79 mg/liter) at 25°C.

The secondary VOC emission from the aqueous cover into the atmosphere is obtained from the following equation:[2]

$$SE_{sa} = K_{il} \quad C_s - \frac{P_i^*}{H_i} \quad .$$

Since P_i^* is negligible, this equation reduces to

$$SE_{sa} = K_{il}C_s \quad ,$$

where

SE_{sa} = the secondary VOC emission rate in g of VOC per m^2 per hr,

K_{il} = the overall liquid mass transfer coefficient in m/hr,

C_s = the chemical concentration in the aqueous cover of the surface impoundment in mg of chemical per liter of aqueous cover (mg/liter is equivalent to g of chemical per m^3 of aqueous cover).

Conversion of SE_{sa} to Mg of VOC emission per year (SE_s)is done in the following example for chemical B:

$$SE_s = (0.099 \text{ m/hr})(79 \text{ g of B/m}^3 \text{ of WW})(1 \text{ Mg of B}/10^6 \text{ g of B})(4047 \text{ m}^2)(8760 \text{ hr/yr})$$

$$= 277 \text{ Mg of secondary VOC emission per year.}$$

In the same manner SE_s for model chemical A is estimated as 0.014 Mg of secondary VOC emission per year.

The capital cost of the plastic cover is \$107.60/m^2 (ref. 1).

The secondary VOC emissions are reduced by 99% by the plastic cover.

The area of the SI to be covered is 4047 m^2.

2. Calculation of Costs and Cost Effectiveness

The net annual costs were calculated to be \$126,300 for each chemical (see Table E-3).

The secondary VOC emissions were calculated to be the following:

Uncontrolled secondary VOC emissions (Mg/hr)	
Chemical A	0.014
Chemical B	277
Controlled secondary VOC emissions (Mg/yr)	
Chemical A	$1.4 \text{ X } 10^{-4}$
Chemical B	2.77
Secondary VOC emisson reduction (Mg/yr)	
Chemical A	0.0139
Chemical B	274

The cost effectiveness for chemical A (see Table E-3) was calculated to be \$9,000,000/Mg (\$126,300 ÷ 0.014 Mg of VOC emission reduced) and for chemical B (see Table E-2) was calculated to be \$460/Mg (\$126,300 ÷ 274 Mg of VOC emission reduced).

G. REFERENCES*

1. Letter from L. P. Hughes, CMA, to D. C. Beck, EPA, Mar. 13, 1980.

2. D. Mackay and P. J. Leinonen, "Rate of Evaporation of Low-Solubility Contaminants from Water Bodies to Atmosphere," *Environmental Science and Technology* **9**(13), 1178—1180 (December 1975).

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an *additional* reference is required for only a certain *portion* of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.